Advances in Organosilicon Chemistry

Edited by M.G. VORONKOV

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Chemistry Series

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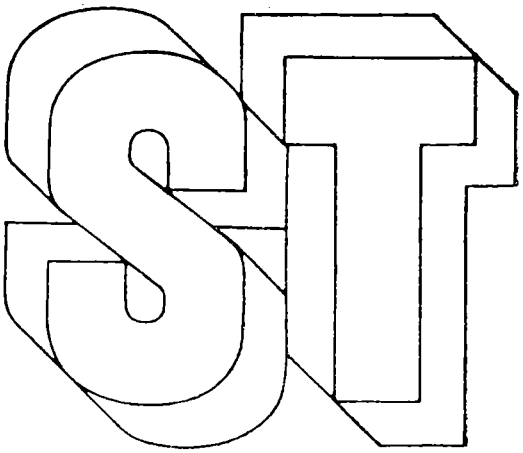

Advances in Organosilicon Chemistry

Edited by
M. G. VORONKOV,
Corr. Mem. USSR Acad. Sci.

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Успехи кремнийорганической химии в СССР
Под редакцией М. Г. Воронкова

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Preface

The earliest work by Russian scientists on the chemistry of organic and organoid compounds of silicon dates back to the period when this science was still in its infancy. As early as 1856-1860, D.I. Mendeleev undertook a detailed study into the synthesis and some reactions of tetraethoxysilane. He was the first to come up with its formula. He was also the first to establish that silicon was tetravalent, putting investigations of silicon's compounds on the right track. Mendeleev was especially interested in volatile silicon compounds because he was convinced that "...they may give an insight into tetratomic radicals and help to explain the role of carbon in many chemical compounds". Finally, Mendeleev was the first to account for the drastic difference between the many oxygen compounds of carbon and silicon, especially, the tendency of the silicon to polymerize. He also pointed out the polymeric nature of inorganic silicon-oxygen compounds, particularly silica, and proposed its correct formula: Si_nO_{2n}.

Mendeleev's theories on the structure of high-molecular organic and inorganic silicon-oxygen compounds assumed them to be similar to polyglycols. His theories were further developed by A.M. Butlerov. In 1879, he derived a formula to explain the formation of so-called "anhydrohydrate" polymeric compounds, that is, products of polycondensation of hydroxyl-containing monomers. Butlerov wrote the world's first textbook "An Introduction to a Complete Course in Organic Chemistry" (1864) describing, among other things, organosilicon compounds.

The theories set forth by Mendeleev and Butlerov, who made a lucid assessment of the relationships between the chemistries of silicon and carbon, were quite advanced. They refuted the hypothesis, prevalent in Western Europe at that time, that stated that the

compounds of these elements are analogous, and denied, in particular, the polymeric structure of oligo- and polysiloxanes [1].

The first systematic studies into the chemistry of organosilicon compounds in the USSR are credited to Academician V.N. Ipat'ev and his student, professor B.N. Dolgov [2]. Their first joint publication in this field appeared in 1929 [3]. In 1933, Dolgov published the first monograph in the world literature dealing with organosilicon chemistry [4]. Apart from a critical review of the wealth of experimental data accumulated by that time, he was the first to appreciate the practical value of organosilicon compounds, and to point out their potential uses in industry and medicine.

In 1937-39, K.A. Andrianov [5] and M.M. Koton [6] published works that laid the foundation of applied organosilicon chemistry in the Soviet Union, and outlined practical applications of polyorganosiloxanes in general. Our chemical industry owes its gratitude to Academician K.A. Andrianov [7] for establishing a new branch specializing in organosilicon monomers and polymers.

In the forties and fifties, intensive research in the chemistry of organosilicon compounds was under way in Moscow and in Leningrad. It was associated with primarily four major schools that were set up by Academicians K.A. Andrianov and A.V. Topchiev, corresponding member of the USSR Academy of Sciences A.D. Petrov, and professor B.N. Dolgov. As regards other prominent scientists who embarked upon research in organosilicon chemistry, mention should be made of corresponding members of the USSR Academy of Sciences A.A. Petrov, M.F. Shostakovsky, and N.S. Nametkin, as well as professors A.L. Klebansky and A.P. Kreshkov. Their efforts have ensured that a major contribution was made by Soviet scientists to the synthetic, theoretical, and applied chemistry of organosilicon compounds.

Works of that period were made familiar to English-speaking readers by a book published in the United States [8] and monographs by Soviet scientists that were translated into English [9-16].

In the second half of this century, fundamental work by Soviet scientists has enriched organosilicon chemistry with such original contributions as polyelementosiloxanes, high-temperature organosilicon synthesis, heterolytic reactions of siloxane bond cleavage, silatranes, biologically active compounds, nitrogen-containing poly-

mers and monomers, silacyclobutanes and polymers based on them, unsaturated organosilicon compounds, reactive intermediates, silicon compounds of phosphorus; sulphur, carbonic acid and its derivatives, organosilicate materials, sorbents, bioprotective coatings, and new materials for microelectronics.

This book summarizes the work carried out in organosilicon chemistry by leading second and third generations of Soviet scientists, most of whom belong to the four schools previously mentioned.

Twelve reviews are presented by these scientists. They cover the results of their own studies and, in general, summarize the state-of-the-art in organosilicon chemistry in the Soviet Union. The book will be of value not only to specialists in the theoretical, synthetic, and applied chemistry of organosilicon compounds, but also to all research workers involved in silicon chemistry, as well as organic and organometallic chemistry.

M.G. Voronkov
Corresponding Member of the USSR Academy of Sciences

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1 Crystal and Molecular Structure of Organosilicon Compounds

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1. INTRODUCTION

Systematic X-ray studies of the crystal and molecular structure of organosilicon compounds (OSC) have been carried out by the authors since the beginning of the 1970s. The largest proportion of these studies involve oligoorganylsiloxanes and in the present review emphasis is put on these compounds. In recent years, in line with modern trends in the synthetic chemistry of OSC, X-ray studies have been more and more frequently done on OSC related to siloxanes, such as silazanes, carbosiloxanes, and organosilicon peroxides. These compounds as well as some nontrivial derivatives of pentacoordinated silicon (silatranes and others) will be discussed.

2. OLIGOORGANYLSILOXANES

In many respects the structural chemistry of oligoorganylsiloxanes is the chemistry of corresponding siloxane cycles [1]. Among acyclic siloxanes, the structure of the branched siloxane, tetrakis(trimethylsiloxy)silane $(Me_3SiO)_4Si$, is determined in our study [2]. The molecule occupies a special position on the two-fold symmetry axis, the average Si—O bond length at the central Si atom (Q unit) is 1.602(3) Å, which is slightly smaller than the average Si—O distance at the peripheral Si atoms (M units) (av. 1.634(3) Å). The average value of the SiOSi angle is 146.0(2)°.

2.1. Monocyclic Oligoorganylcyclosiloxanes

We start the discussion of the structure of oligoorganylcyclosiloxanes with their simplest representatives, cyclotrisiloxane derivatives.

Table 1 lists the most important structural parameters of the D_3 trisiloxane cycles and their analogues. These cycles are almost planar, the maximum deviation of the cycle atoms from their mean plane (Δ) not exceeding 0.1 Å.

In molecules of oligoorganylcyclosiloxanes $(RR'SiO)_n$ with $n > 3$ the cycles are not planar (Table 2). A comparison of the data given in Tables 1 and 2 shows that shorter Si—O bonds (av. 1.62 Å and 1.65 Å, respectively) and larger SiOSi bond angles (142-149° and 131-134°) are characteristic for tetrasiloxane cycles as compared

Table 1. Geometrical Parameters of Trisiloxane Cycles in Monocyclotrisiloxanes (l: average Si—O bond length, Å; α: average SiOSi bond angle, °; Δ: maximum deviation of atoms from the cycle plane, Å)

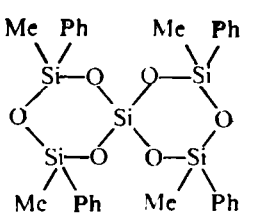
Compound	Formula	l	α	Δ	References
I	$(Ph_2SiO)_3$	1.64	131.9	0.07	[3]
II	*cis*-$(MePhSiO)_3$	1.65(1)	132(2)	0.10	[4]
III	*trans*-$(MePhSiO)_3$	1.65(1)	132(2)	0.05	[5]
IV	$Na_3[PhSi(O)O]_3 \cdot 8H_2O$	1.647(0)	133(1)	0.029	[6]

with trisiloxanes. The tetrasiloxane cycles, which by their shape belong to the BB-B family, were deformed approximately twice as much as the cycles of the C—LC family. The *trans*-conformers VIIA and VIIB are an exception; the presence of small "substituents" as H atoms at Si atoms favours a more significant cycle deformation.

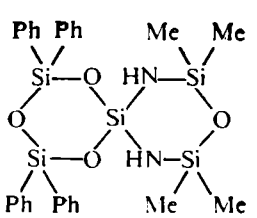
2.2. Oligoorganylspirocyclosiloxanes

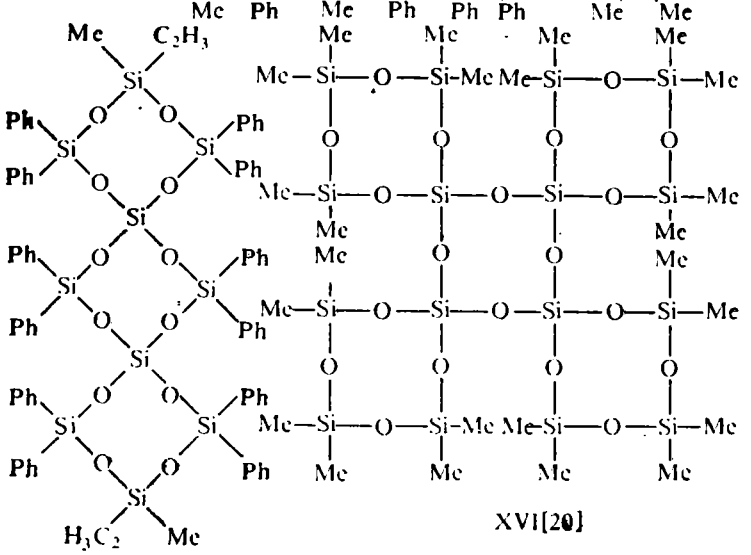
The structures of six oligoorganylspirocyclosiloxanes, XII to XVII, have been determined. The Si—O bonds of the spiro

XII[16]



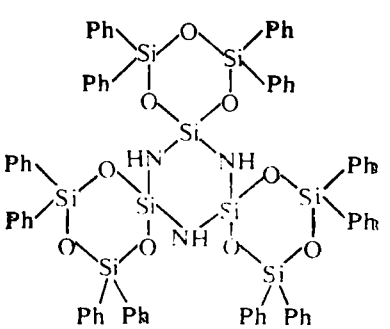
XIII[17]



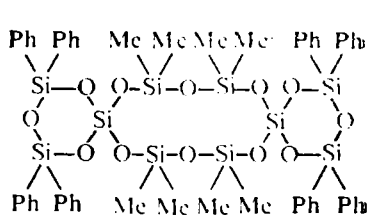


XV[19]

XVI[20]

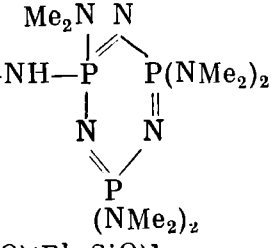


XIV[18]



XVII[21]

Table 2. Geometrical Parameters of Tetrasiloxane Cycles in Monocyclotetrasiloxanes (l—average Si—O bond length, Å; α—average SiOSi bond angle, °; Q—square root of the sum of squares of the deviations of atoms from the cycle plane, Å)*

Compound	Formula	Cycle configuration	l	α	Cycle conformation	Q	References
V	*cis*-$[(Me_2SiO)(Ph_2SiO)]_2$	D_4	1.62	148.5	(C—LC) → S_4'	0.993	[7]
VI	$(Me_2SiO)(Ph_2SiO)_3$	D_4	1.61	146.2	B	1.112	[8]
VIIA	*trans*-$\{[H(Me)SiO](Ph_2SiO)\}_2$	D_4	1.603	147.5	LC	1.022	[9]
VIIB		D_4	1.630	149.5	C → LC	1.433	
VIIC		D_4	1.612	151.2	BB → (LC—CR)	1.246	
VIII	$[(Me_2SiO)_3(Me(R)Si)]$ 	D_4	1.62	143.2	B	1.172	[10]
IX	*cis*-$[(Me(HO)SiO)(Ph_2SiO)]_2$	D_2T_2	1.622	144	BB—B	1.187	[11]
XA	*trans*-$[\{(HO)_2SiO\}(Ph_2SiO)]_2 \cdot Py$	D_2Q_2	1.612(2)	148.4(5) 156.7(5)	C → LC	0.471	[12]
XB		D_2Q_2	1.610(2)	150.4(5) 156.5(5)	C → LC	0.397	
XIA	*trans*-$[\{[Me_2(HO)Si]_2SiO\}(Ph_2SiO)]_2$	D_2Q_2	1.60(1)	148.2(7) 166.2(7)	LC—S_4'—CR	0.342	[13]
XIB		D_2Q_2	1.61(1)	146.5(6) 157.6(7)	LC—D_2	0.565	

* See the meaning of the cycle conformation nomenclature in Ref. [14]; two isomers (three conformers) of the VII compound coexist in crystal; crystals of X and XI are built of two independent molecules.

units are slightly shortened, which indicates their higher strength. The trisiloxane cycles in spirosiloxanes retain their planar geometry. The central Q_4 cycle of the pentacyclic XVI molecule is quite flat, the maximum deviation of its atoms from the plane being $\Delta = 0.096$ Å. The planarity of the cycle is presumably due to steric reasons, viz. to short intramolecular contacts (O(1)...Si(6) 3.835(6) Å

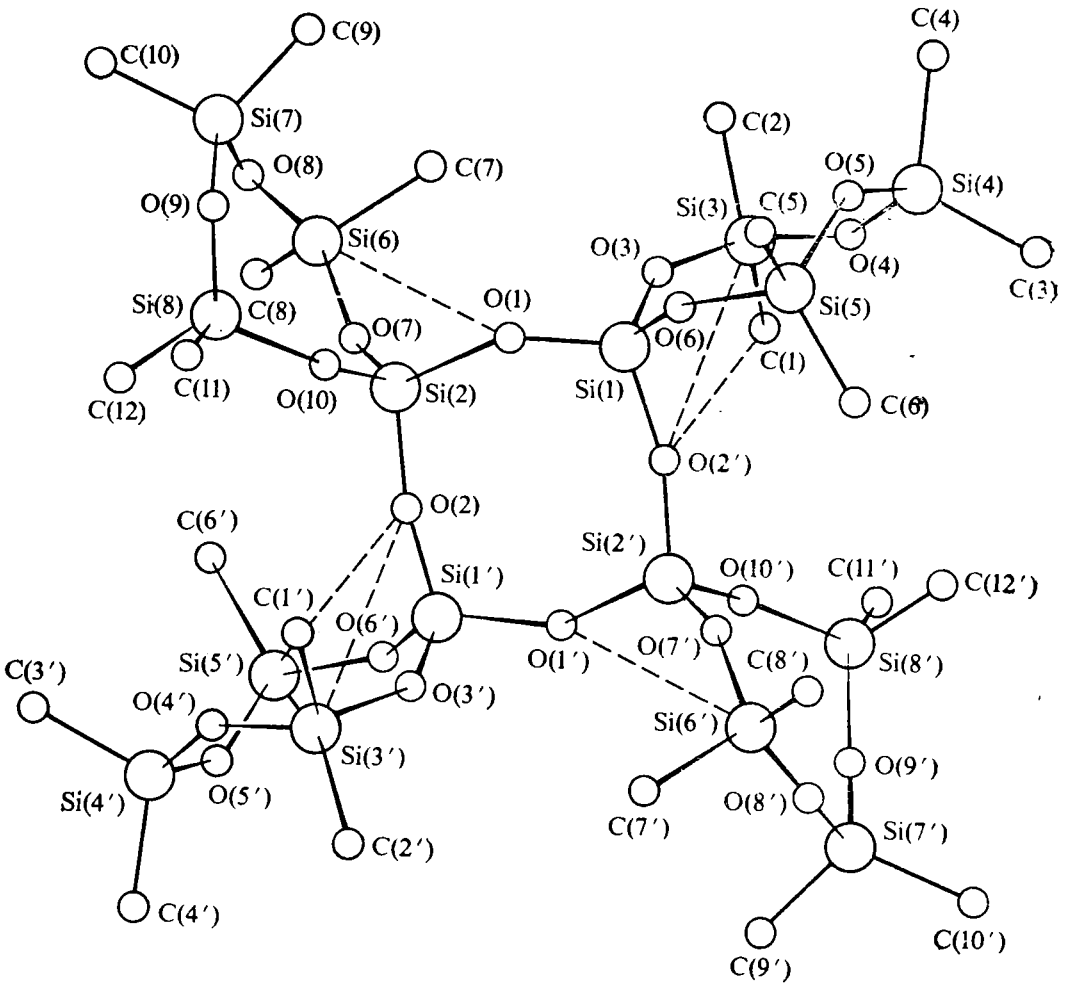


Figure 1. Structure of molecule XVI (C_i symmetry). Non-bonded O...Si contacts responsible for the almost planar shape of the Q_4 cycle are shown [20].

O(2)...Si(3) 3.700(6) Å, O(2)...Si(5) 3.704(6) Å (Fig. 1)) which are close to the sum of the van der Waals radii of Si and O (3.62 Å). In accordance with the distribution of nonvalent contacts, the Si(1')O(2)Si(2) bond angle (166.9(4)°) in the Q_4 cycle is noticeably larger than the Si(1)O(1)Si(2) angle (148.8(4)°).

The planarity of the tetrasiloxane cycle is significant since a more planar shape of the cycle is caused by larger values of the oxygen bond angles. At the same time, there is a correlation between the SiOSi

bond angle and the Si—O bond length, viz. on increasing SiOSi angles Si—O bonds become shorter and their strength increases. Strengthening of the S—O bond is also favoured by the coordination

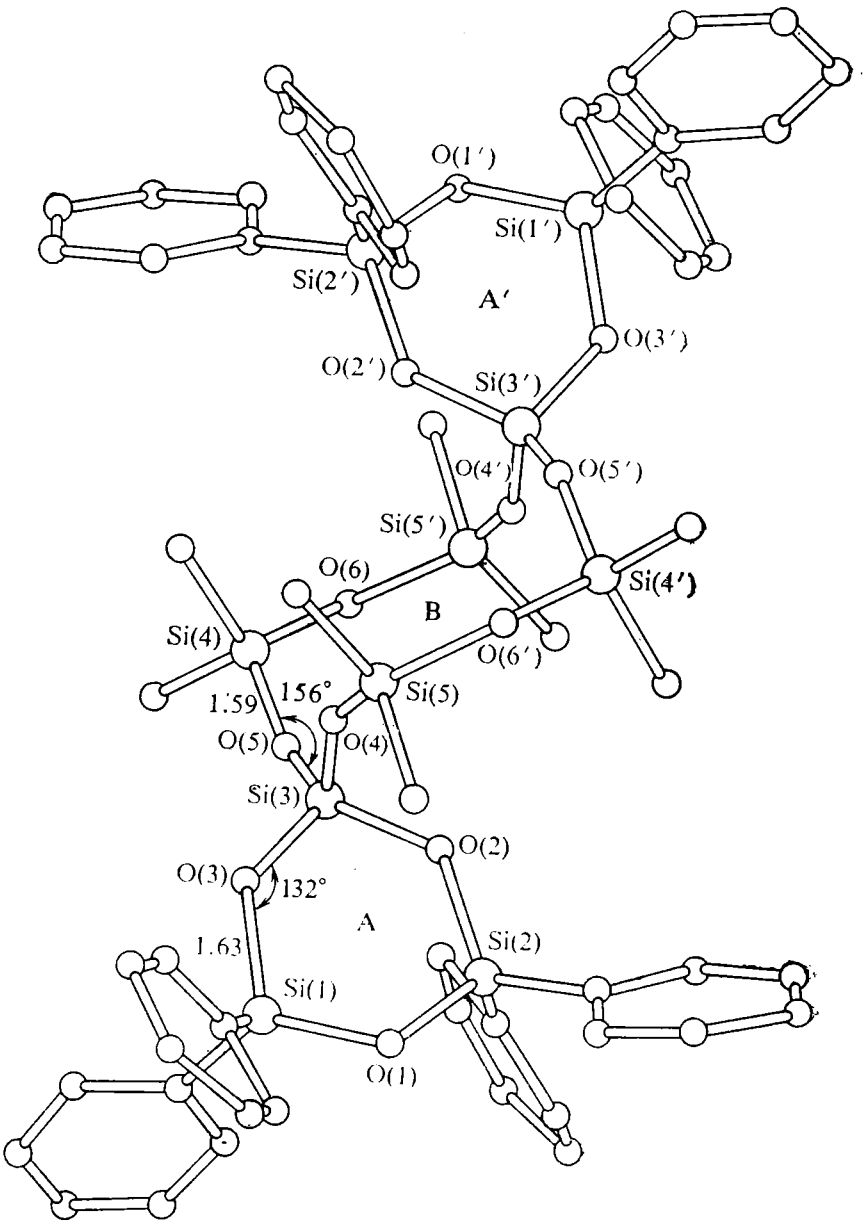


Figure 2. Structure of molecule XVII (C_i symmetry) [21].

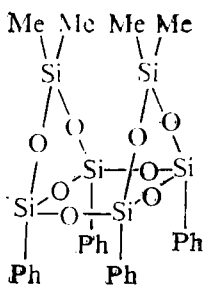
of Si atoms in the spiro units by four oxygen atoms [1]. Hence, the siloxane bonds in a polyspirocyclic polymer whose elementary units are similar to the central cycle of the XVI molecule should be stronger than in ordinary polyorganylsiloxanes.

The 12-membered D_4T_2 cycle in XVII (Fig. 2) has a normal chair conformation: eight atoms of the cycle (Si(4), Si(5), Si(4'), Si(5'),

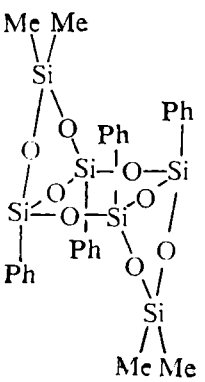
O(4), O(6), O(4′), and O(6′)) are situated almost in one plane, with the bending of the "back" of the chair (i.e. the Si(3), Si(4), O(4), O(5) and Si(3′), Si(4′), O(4′), O(5′) planes) equal to 78°.

2.3. Cyclolinear Oligoorganylsiloxanes

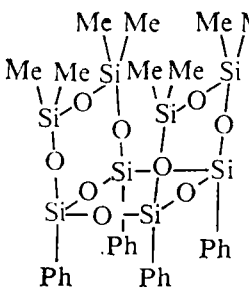
The most interesting feature of the tricyclic molecules of XVIII-XXI is the geometry of the inner cycles which can be considered as the elementary units of cyclolinear polyorganylsilsesquioxanes. In the *cis*-tricyclic units of XVIII and XX (Fig. 3), the shape of the inner cycle is similar to LB [14], and in the *trans*-tricyclic units of XIX and XXI, similar to LC. According to force field calculations [26], fusion of additional siloxane cycles to both



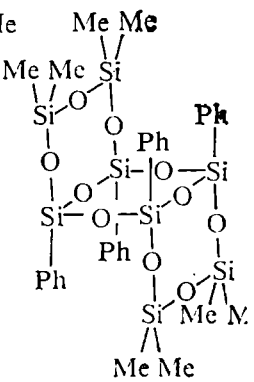
XVIII[22]



XIX[23]



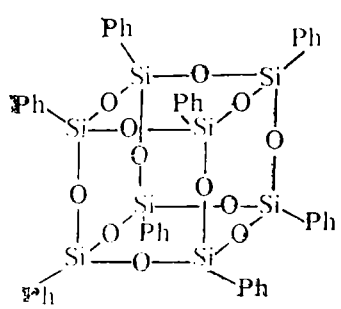
XX[24]

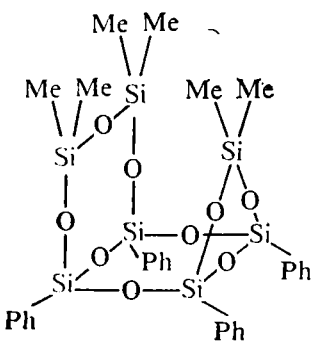


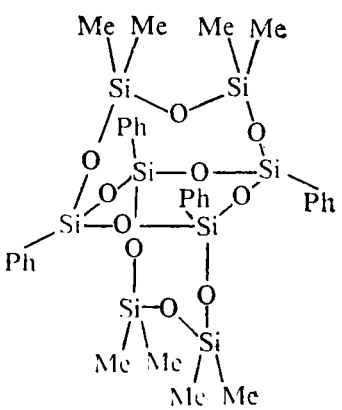
XXI[25]

sides of the XVIII-XXI molecules does not alter the conformation of the inner T_4 cycles in these systems.

The crown conformation (CR), in a series of cisoid molecules going from a closed cubane-like molecule of $(PhSiO_{1.5})_8$ (XXII) [27] to molecule XXIII with an "enlarged" cubane (Fig. 4) [28] and, finally, to an "opened"







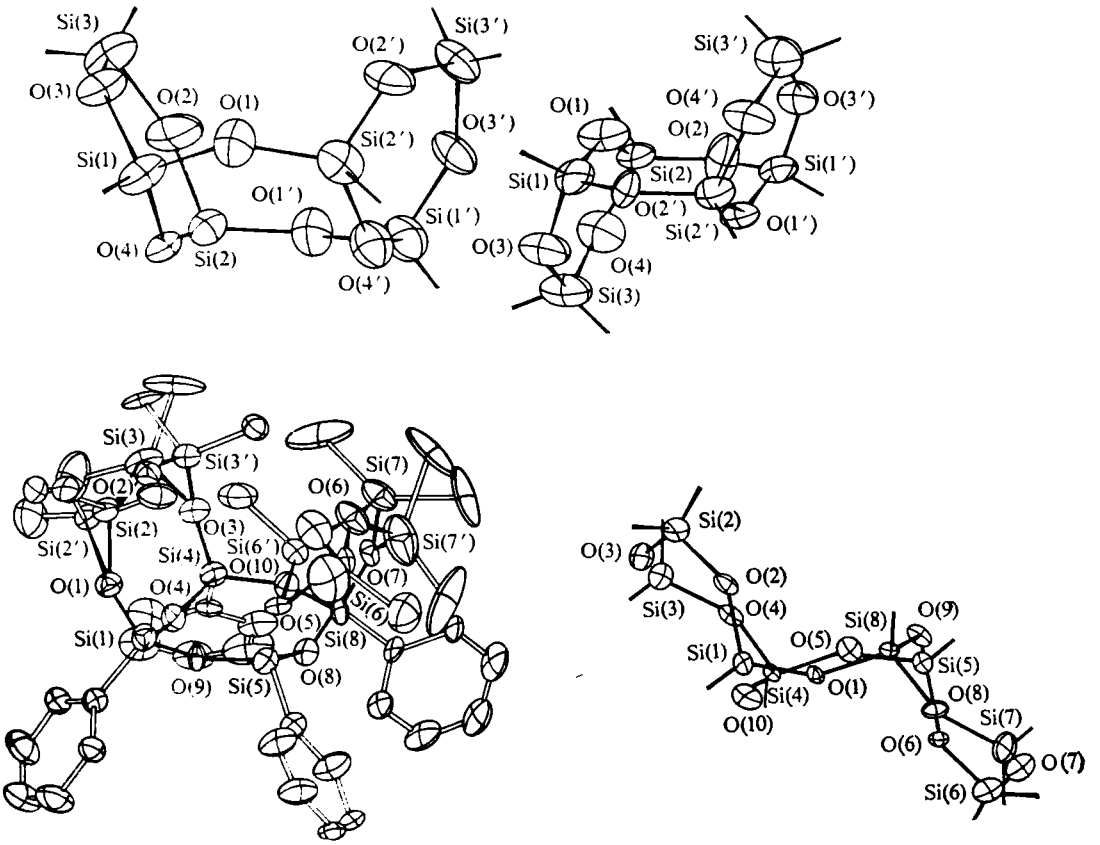


Figure 3. Geometry of the siloxane frameworks of molecules XVIII-XXI [22-25].

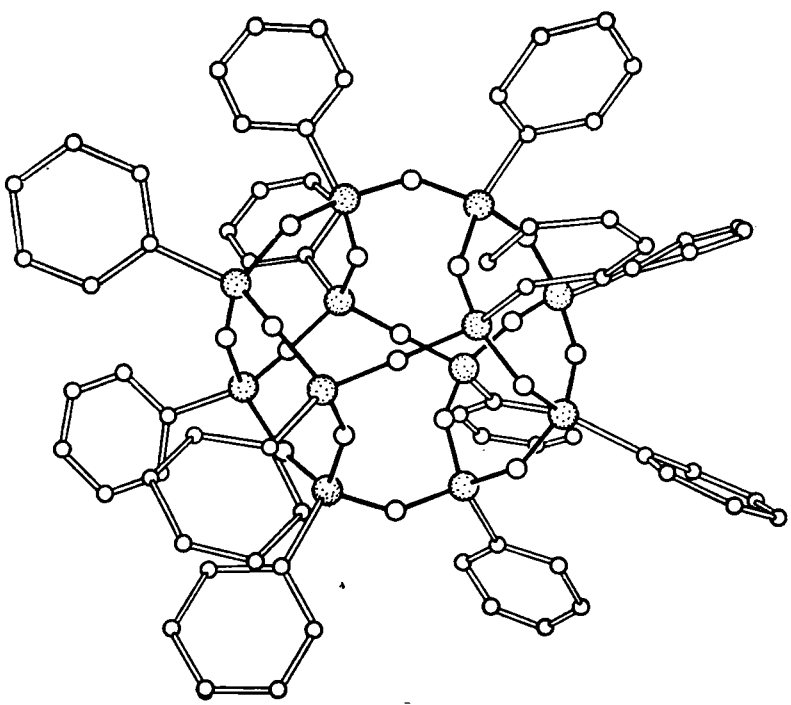


Figure 4. Structure of molecule XXIII (S_4 symmetry) [28].

cubane (XX) structure, gradually decreases its contribution to the shape of the inner T_4 cycle from 43% (XXII) to 24% (XX) [14]. In going from the cubane-like frameworks of XXII and XXIII to the "opened" forms of XX and XXIV, the cyclic system becomes bent along the lateral O...O median line of the inner cycle (e.g. O(1)...O(5) in XXIV (Fig. 5)); alongside with a helical twisting of both these molecules (by abt. 20° in XXIV) round the longitudinal axis (i.e. the other median line of the inner cycle, e.g. O(8)...O(9) in XXIV).

Involvement of 10-membered cycles into the rather complex polycyclic system of XXV molecule undoubtedly exerts [an

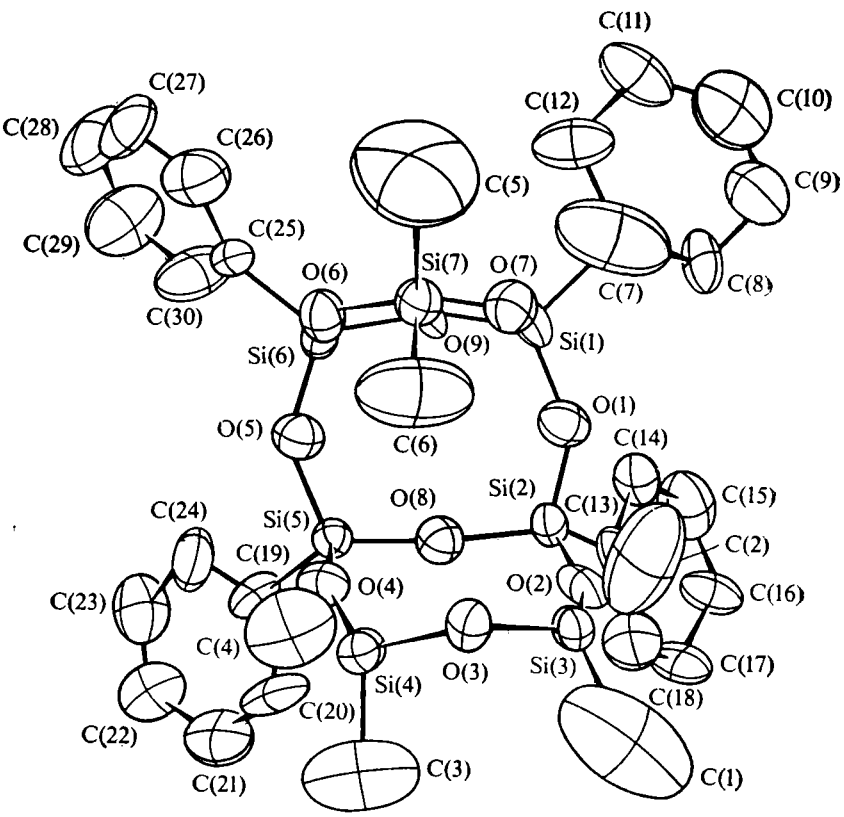


Figure 5. Structure of cisoid molecule XXIV [29].

effect on their geometry (Fig. 6) [25]. The "chelate" semicycles, Si(1)O(5)Si(5)O(6)Si(6)O(7)Si(3) and Si(2)O(8)Si(7)O(9)Si(8)O(10)Si(4) have a practically planar structure (atomic deviations from the corresponding mean planes by no more than 0.2 Å). Note the "concave" arrangement of the atoms O(6) and O(9) which are shifted to the centre of the molecule with respect to the Si...Si lines that join the adjacent Si atoms. Such a 10-membered bridging semicycle structure was observed earlier [30] and is probably a general feature of

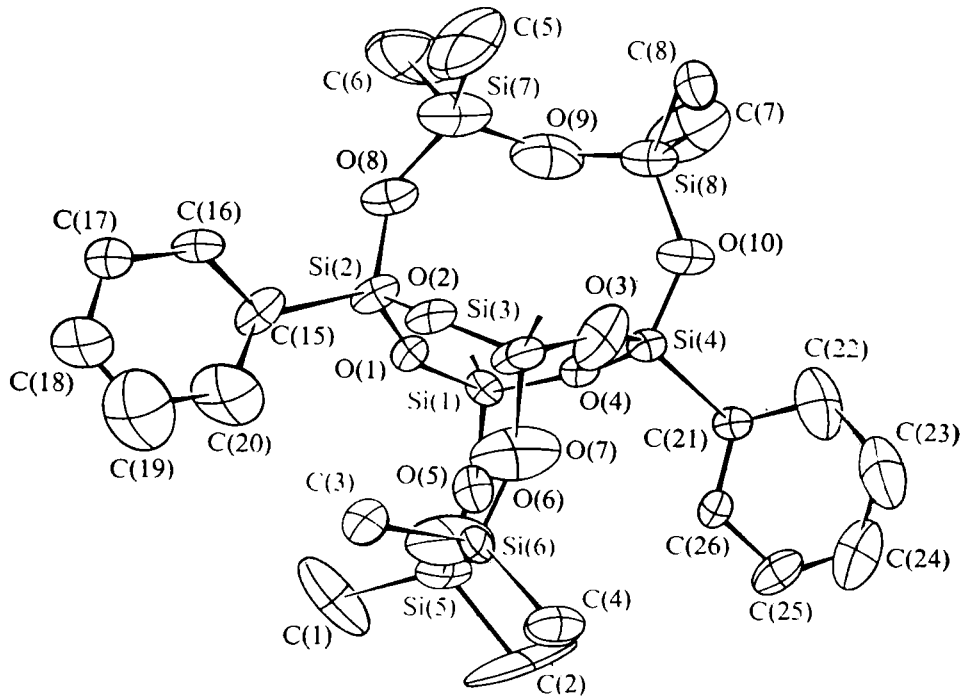


Figure 6. Structure of molecule XXV [25]. Ph substituents are omitted for clarity.

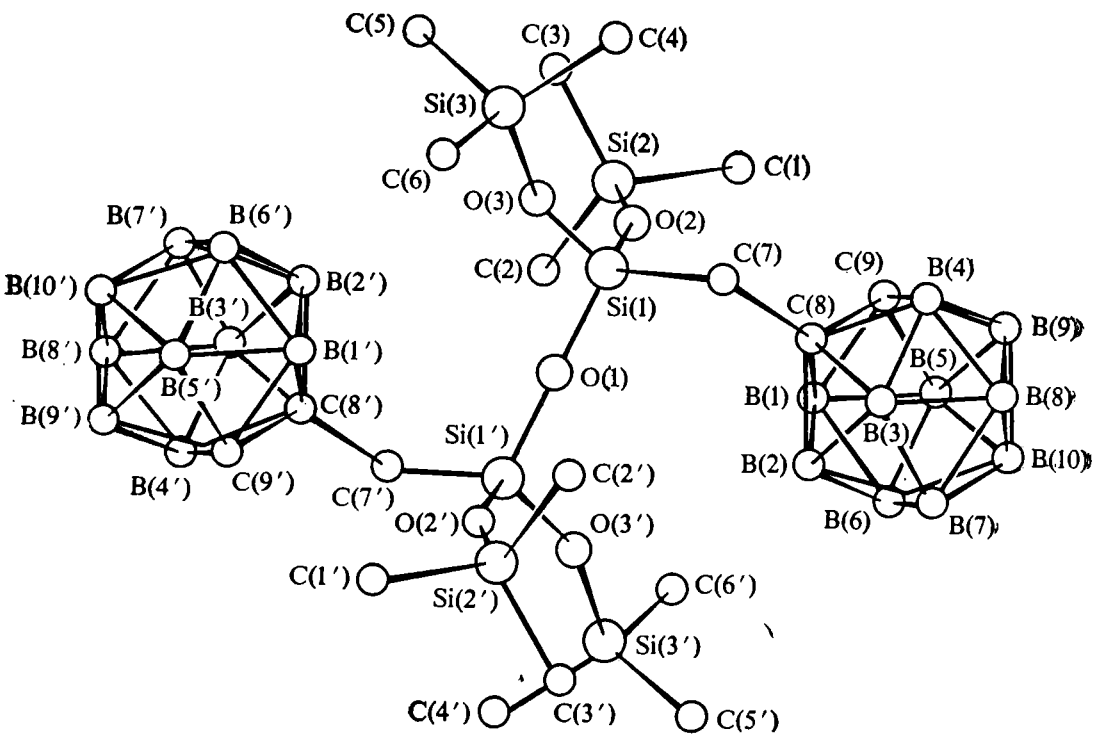


Figure 7. Structure of molecule XXX (C_i symmetry) [33].

"diagonal" siloxane bridges. The Si(5)O(6)Si(6) and Si(7)O(9)Si(8) bond angles (161.3 and 154.3(4)°) are not much larger than the other SiOSi bond angles in the molecule XXIV (139.2 and 156.9(4)°).

2.4. Linear O Bridges in Hexaorganyldisiloxanes

One of the "anomalies" of siloxane geometry is the presence of linear O bridges in some hexaorganyldisiloxanes (Fig. 7, Table 3). There are no less than five explanations of this geometry [33], the most probable of them involves electronic factors [34].

Table 3. Bond Lengths d (Å) in Linear Hexaorganyldisiloxanes

Compound	Formula	d	References
XXVI	$(Ph_3Si)_2O$	1.616	[30]
XXVII	$(Ph_3Si)_2O$*	1.618(4)	[19]
XXVIII	$[(CF_3CH_2CH_2)_3Si]_2O$	1.60	[31]
XXIX	$[(tert\text{-}BuO)_3Si]_2O$	1.589(1)	[32]
XXX	$[(Me_3SiO)_2(HCB_{10}H_{10}CCH_2)Si]_2O$	1.596(1)	[33]

* In crystal of the $(Ph_3Si)_2O \cdot 2C_6H_6$ solvate.

2.5. Intermolecular Distances, Ionic Interaction, and Hydrogen Bonds in Oligoorganylsiloxane Crystals

According to intermolecular contacts found in crystals of oligoorganylsiloxanes [35] the molecules of "non-rigid" siloxanes occupy a larger effective volume than the volume defined by generally accepted van der Waals radii. The larger effective volume is in agreement with the more intense thermal vibrations of the molecules of "non-rigid" siloxanes. On the other hand, intermolecular contacts in crystals of the more rigid siloxanes whose molecules have bulky substituents or are "fixed" by intermolecular hydrogen bonds have distances that are normal for organic crystals. This results in "rigid" and "non-rigid" siloxane crystals [35] having different packing densities.

Ionic oligoorganylsiloxanes are interesting because their structures provide information about the intermediates frozen in crystals or about a transition state of the siloxane ionic polymerization.

The planarity of the trisiloxane cycle of the $[PhSi(O)O]_3^{3-}$ anion in the crystal of IV is even more apparent than in nonionic cyclotrisiloxane derivatives (Table 1). It is useful to note a marked shorten-

ing of the exocyclic Si—O⁻ bonds. As in a number of other ionic organic compounds, in the crystal of IV an isolated arrangement of the structural elements involving ionic and van der Waals interaction is thermodynamically favourable (Fig. 8). The crystal is made up of layers of two types: hydrophobic layers formed by phenyl

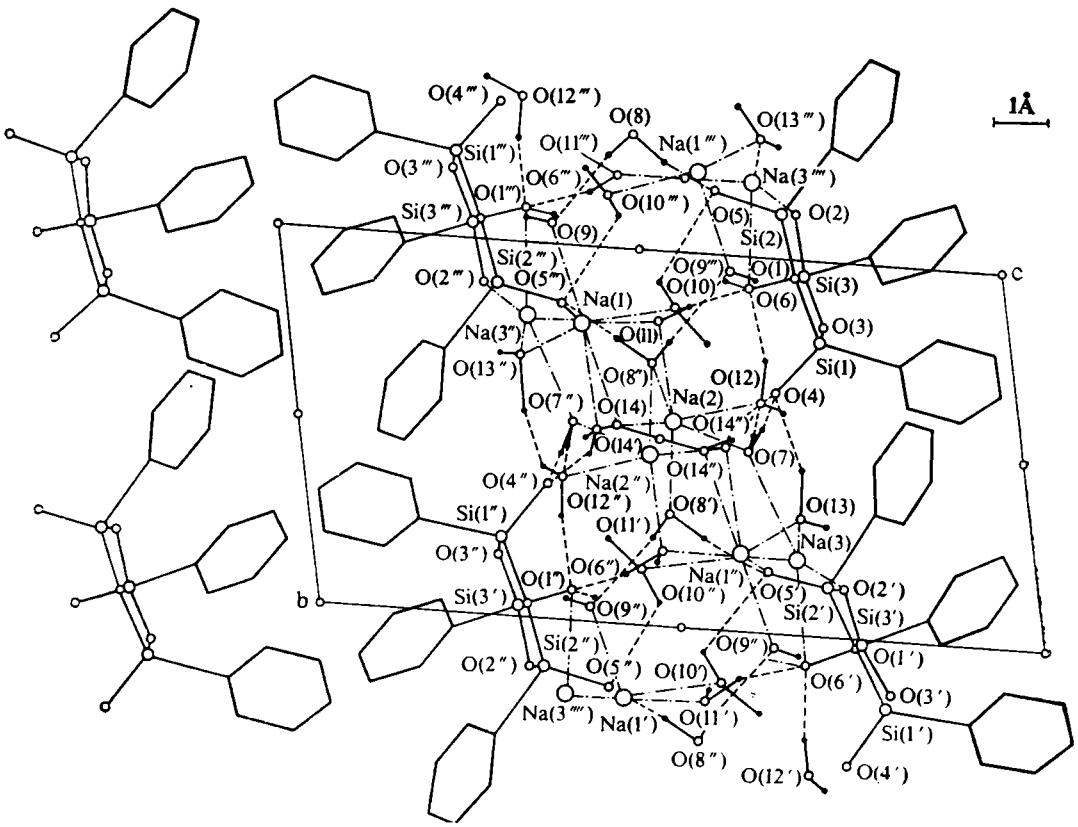


Figure 8. Crystal structure of IV. Hydrogen bonds are shown by dotted lines, the coordination of Na^+, by dot-and-dash lines [6].

substituents directed to each other (van der Waals interaction) and hydrophilic layers (ionic interaction and hydrogen bonds). Other siloxanolates and silanolates of alkali metals, for example $[Na(Me_3SiO)]\cdot 3H_2O$ and $Na_2[(Me_2SiO)_2O]\cdot H_2O$ [36], are built on the same principle of segregation of van der Waals and electrostatic interactions.

At the same time, a crystal of an anhydrous complex of sodium trimethylsilanolate and sodium hydroxide (XXXI) is built of the closed "clathrate" associates of the $10Me_3SiONa\cdot NaOH$ composition (Fig. 9) [37]. This island structural type is a result of a deficiency of electron donors (in particular, water molecules). The O atoms of silanolate anions are situated inside the associate and the methyl groups are directed outwards, thus forming the non-polar shell of

the "cluster". The O atom of the hydroxyl group located near the centre of the associate is surrounded by five Na^+ cations. Inside the associates electrostatic interaction between the ionized O^- atoms of the anions, the Na^+ cations, and the hydroxyl group is stronger than, for example, in the hydrated salt $[Na(Me_3SiO)]\cdot 3H_2O$ [36].

Oligoorganylsiloxanes can form intermolecular hydrogen bonds with external proton donors (phenol, water, alcohols, etc.). If hydrox-

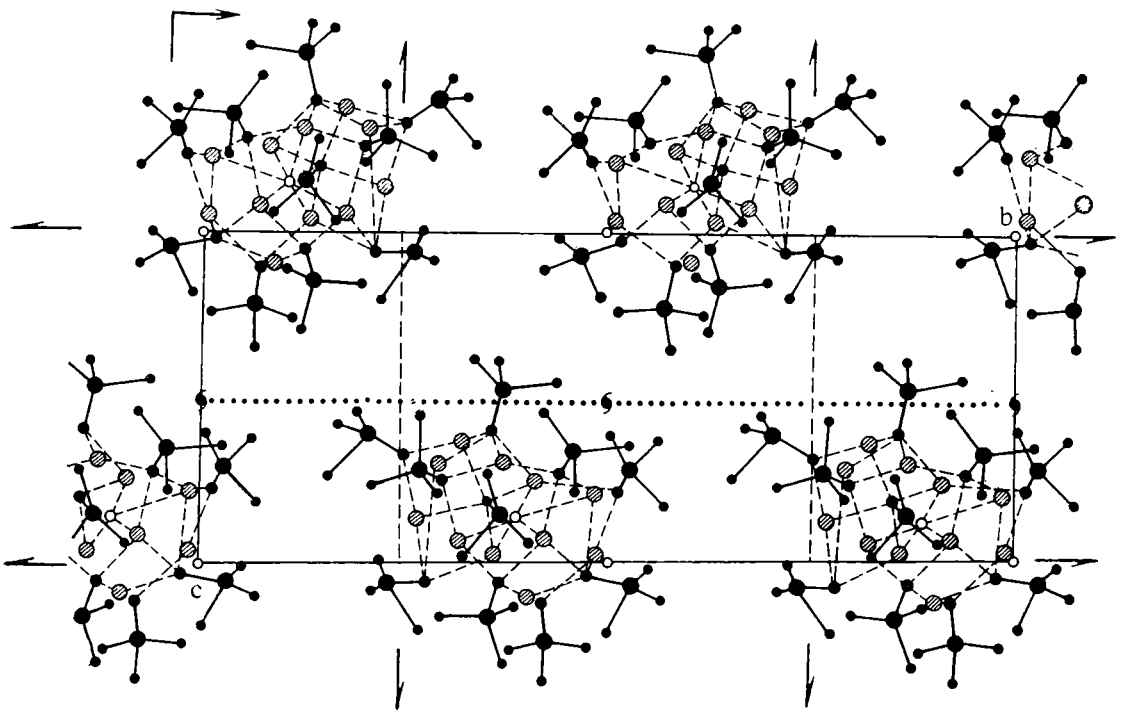


Figure 9. Crystal of $10Me_3SiONa\cdot NaOH$ built of "cluster" associates, each of these involving $10Me_3SiO^-$ anions, $11Na^+$ cations, and one HO^- anion (· denotes C atom, • O atom, ●Si atom, ◍ Na atom, ○ O atom of the HO group). Dotted lines: ionic interaction Na...O [37].

yl groups (olygoorganylsiloxanols) are present in siloxane molecules, then silanol groups act both as donors and as acceptors in the intermolecular hydrogen bonds.

Hydrogen bonds of the first type (O—H...O with participation of H_2O molecules) exist in the hydrophilic layers of crystals of XXXI and IV (Fig. 8). All these hydrogen bonds are of medium strength [6].

Figure 10 gives an example of the crystal structure of organylsiloxane X in which hydrogen bonds are formed by silanol groups acting as proton donors. Each of the two symmetrically unique molecules X forms strong O—H...N hydrogen bonds with the two Py solvate

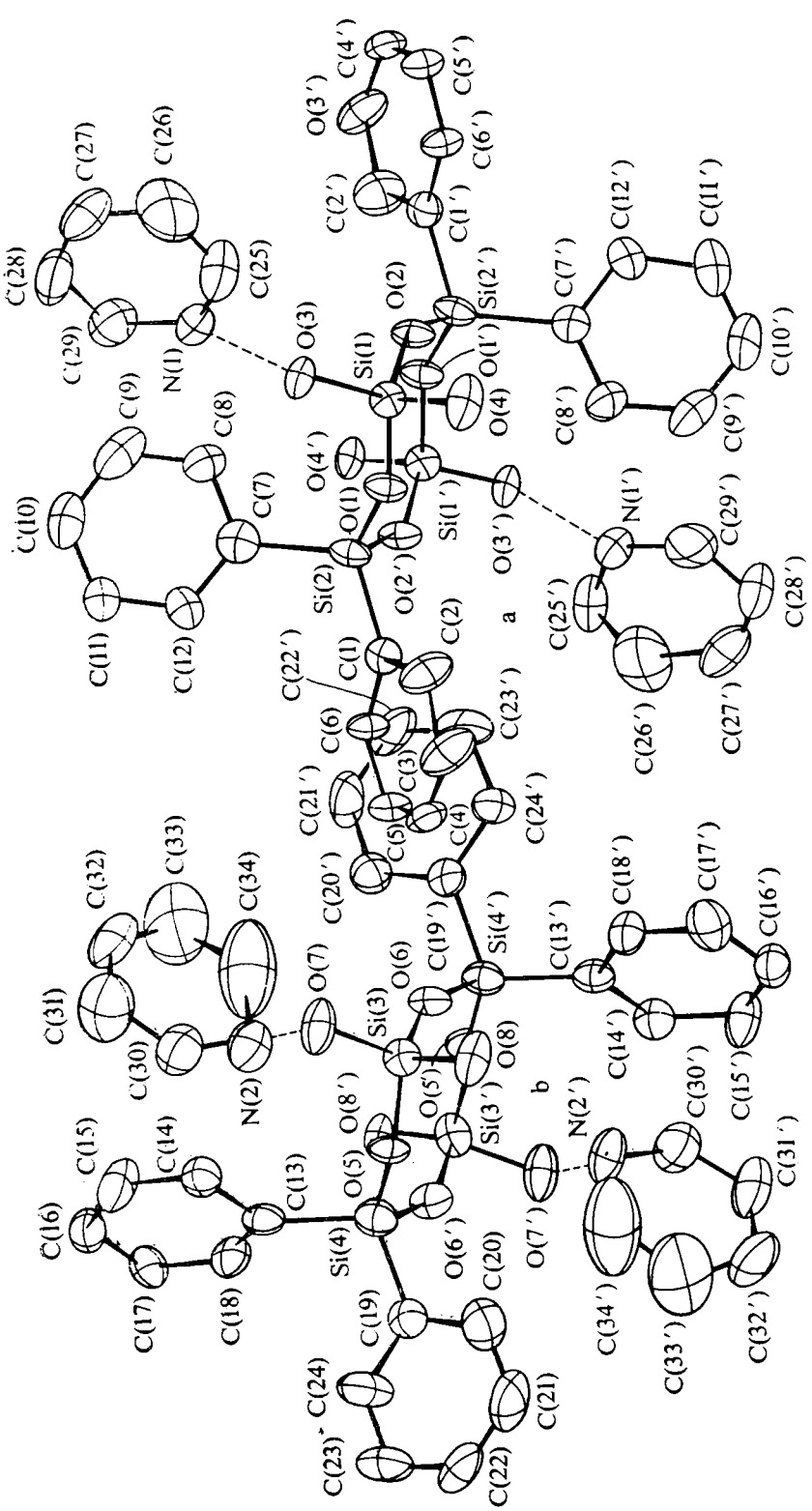


Figure 10. Arrangement of the $[\{(HO)_2SiO\}(Ph_2SiO)]_2 \cdot Py$ complexes in crystal. Dotted lines show the O—H...N hydrogen bonds between two independent molecules and two independent Py solvate molecules [12].

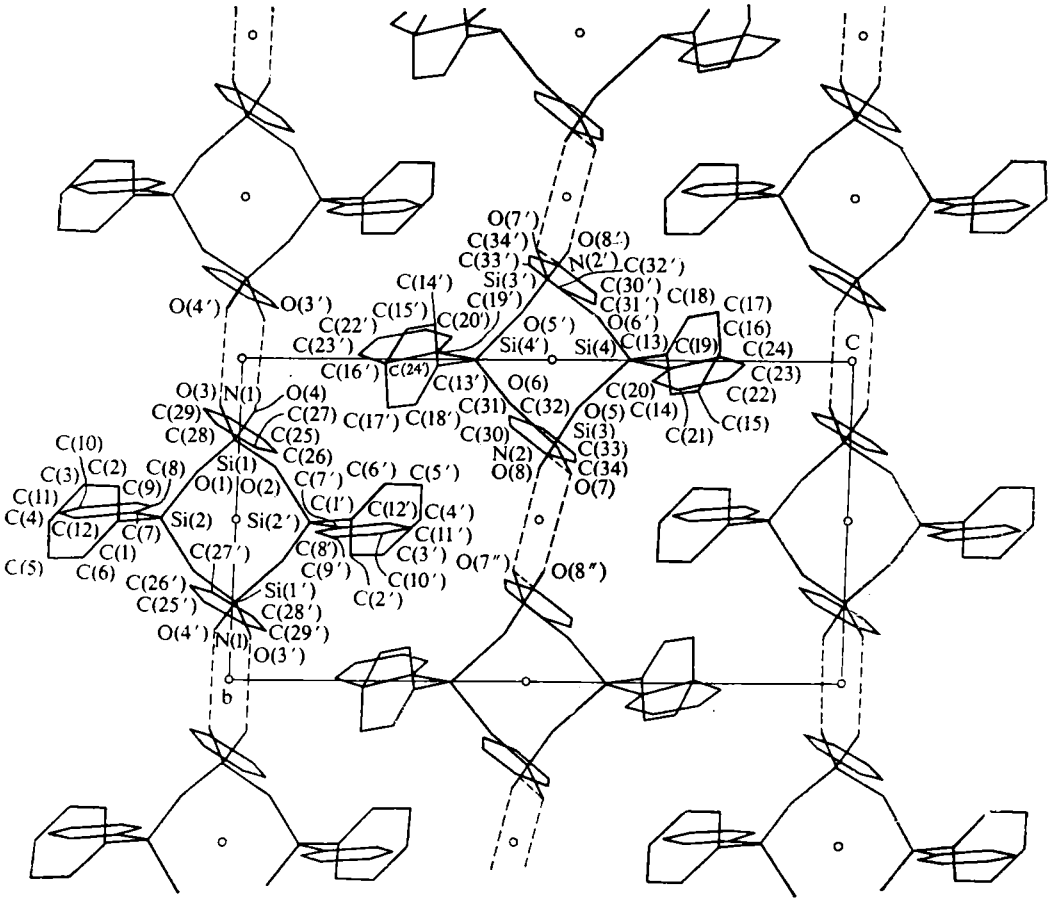


Figure 11. Crystal structure of X. Hydrogen bonds are shown by dotted lines [11].

molecules. The X crystal (Fig. 11) also has two more systems of hydrogen bonds (O—H...O) of medium strength joining the molecules into endless chains [12].

3. OLIGOORGANYLCYCLOSILAZANES

Among the classes of OSC related to siloxanes, silazanes and oxasilazanes have been studied most thoroughly.

4-Membered disilazane cycles, $(SiN)_2$, have a planar structure with the endocyclic bond angles at the N atoms being 1-2° larger than at the Si atoms. This means that the diagonal Si...Si distances in the cycles are slightly larger than the N...N distances (2.492(1) and 2.438(4) Å in XXXII (Fig. 12) [38]) owing to the larger size of the Si atoms. Repulsion of the Si atoms is also responsible for elongation of the endocyclic Si—N bonds in dicyclosilazane derivatives as compared with the exocyclic Si—N bonds (1.738 and 1.708(3) Å in XXXII).

The 4-membered cycle in another representative of small silicon-containing heterocycles, $(Me_2SiS)_2$, is also planar. The SSiS bond angles are larger than the SiSS angles (97.54(7) and 82.46(6)°, respectively) although the Si—S distances in this molecule (2.152(2) Å) are very close to those observed in other oligoorganylcyclosilthianes [39].

Depending on the substituents, trisilazane cycles may be planar (the maximum deviation of the atoms in the molecule XXXIII

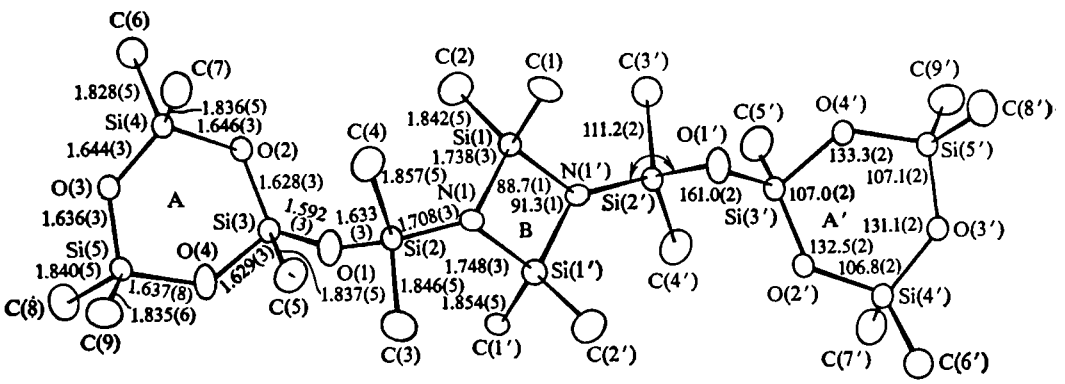
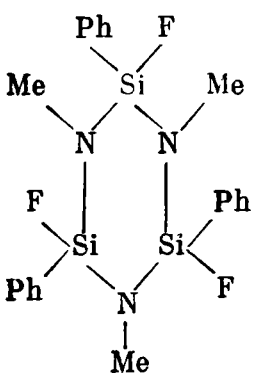


Figure 12. Structure of molecule XXXII (C_i symmetry) [38].

from the mean cycle plane is 0.05 Å [40]) and noticeably non-planar (the deviation of the atoms in the molecule XIV from the silazane cycle plane is 0.15 Å, sofa conformation). The endocyclic Si—N distances in the molecules XIV and XXXIII are identical (1.69(1) and 1.700(6) Å, respectively).



XXXIII

The tetrasilazane cycle of tetramethyltetraphenylcyclotetrasilazane, $[(PhMeSi)(NH)]_4$, has the LC conformation [41] and is much more deformed (the square root of the sum of the squares of the deviations of its atoms from the mean cycle plane, Q, is 2.674 Å) than the tetrasiloxane cycle of monocyclotetrasiloxanes (Table 2). The 8-membered 1,5-dioxacyclotetrasiloxane ring of the molecule

$[(PhMeSi)_4(NH)_2O_2]$ (XXXV) is slightly less deformed ($Q = 1.804$ Å), the general conformation also being the LC type [42].

Three equivalent tetrasilazane cycles of the molecule XXXVI (Fig. 13) [43] are bent along the N(1)...N(2) line and have a complicated shape described as LC → BB ← CR. The degree of deformation of the cycles is only slightly different from that of monocyclotetrasiloxanes (Table 2).

The Si—N distances in cyclotetrasilazanes (1.72(1) Å in XXXIV and 1.71(1) Å in XXXV) are not greatly different from those observed

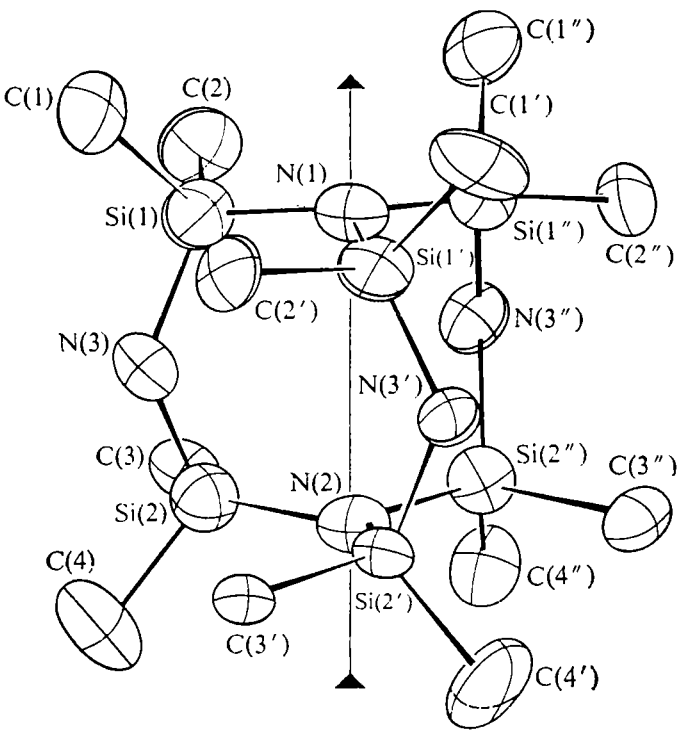


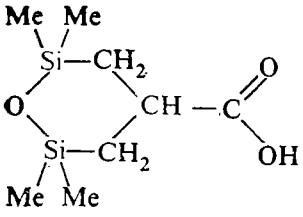
Figure 13. Structure of molecule XXXVI (C_3 symmetry) [43].

in cyclotrisilazanes. In the more sterically strained XXXVI molecule the Si—N distances are somewhat larger (1.749(5) Å), the Si—N distances at the secondary and tertiary N atoms of the XXXVI molecule are identical.

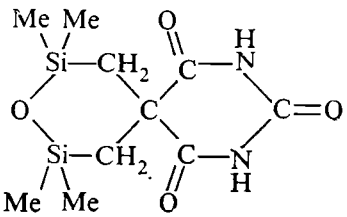
4. OLIGOORGANYLCYCLOCARBOSILOXANES

The SiOSi bond angles (130.1(2)-132.9(3)°) and the Si—O bond lengths (1.630(3)-1.640(3) Å) in the 6-membered carbosiloxane cycles of the molecules XXXVII-XXXIX are unexceptional. In

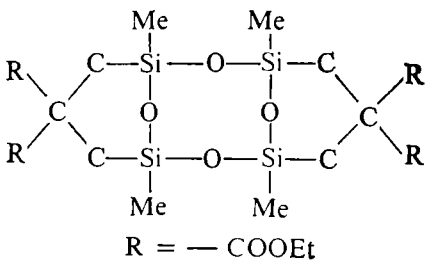
XXXVII and XXXIX these cycles have



XXXVII[44]



XXXVIII[45]



XXXIX[45]

a sofa conformation and in XXXVIII that of a distorted boat.

The carbosiloxane framework in the transoid molecule XXXIX (Fig. 14) is rigid. In solution, according to force field calculations only rotations of carboethoxy groups are possible [45].

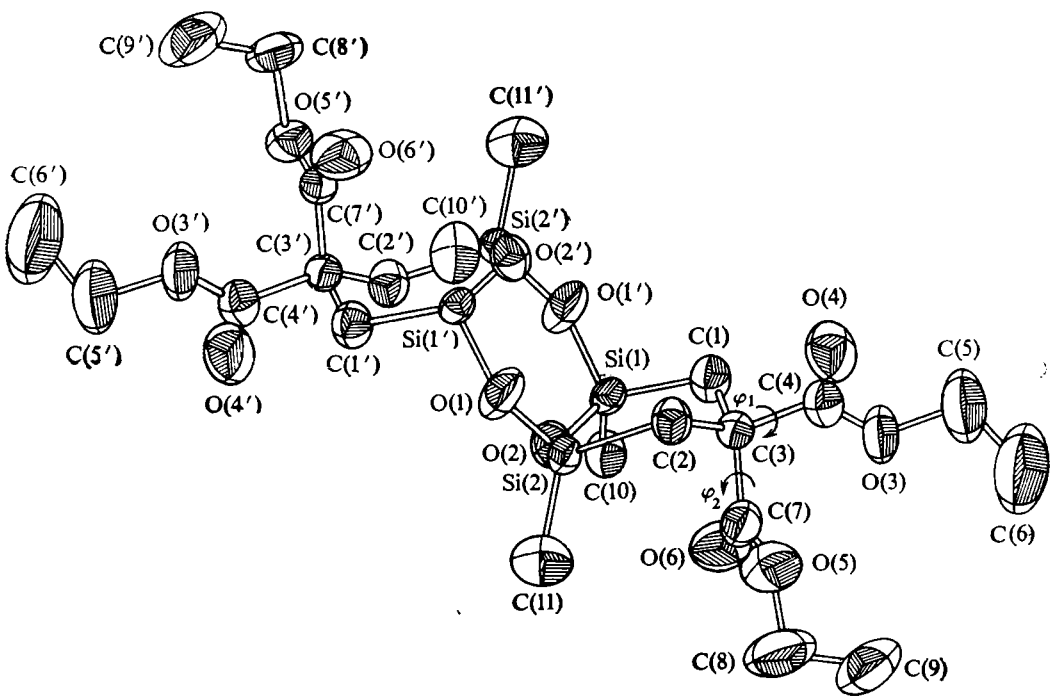


Figure 14. Structure of molecule XXXIX (C_i symmetry) [45].

The reasons for a high stability of the carbosiloxanes XXXVIII and XXXIX to the action of ionic agents should be probably sought for in the electron density redistribution at the Si and O atoms, caused by introducing functional groups into the organic surrounding [45].

5. ORGANOSILICON PEROXIDES

Organosilicon peroxides have aroused interest because of their ability to decompose into radicals and to undergo unusual rearrangements [46].

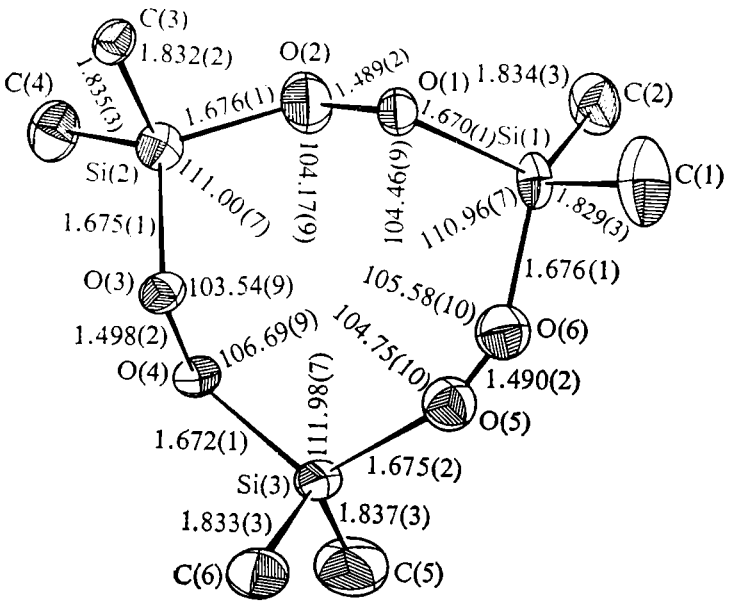


Figure 15. Structure of molecule XLV [51].

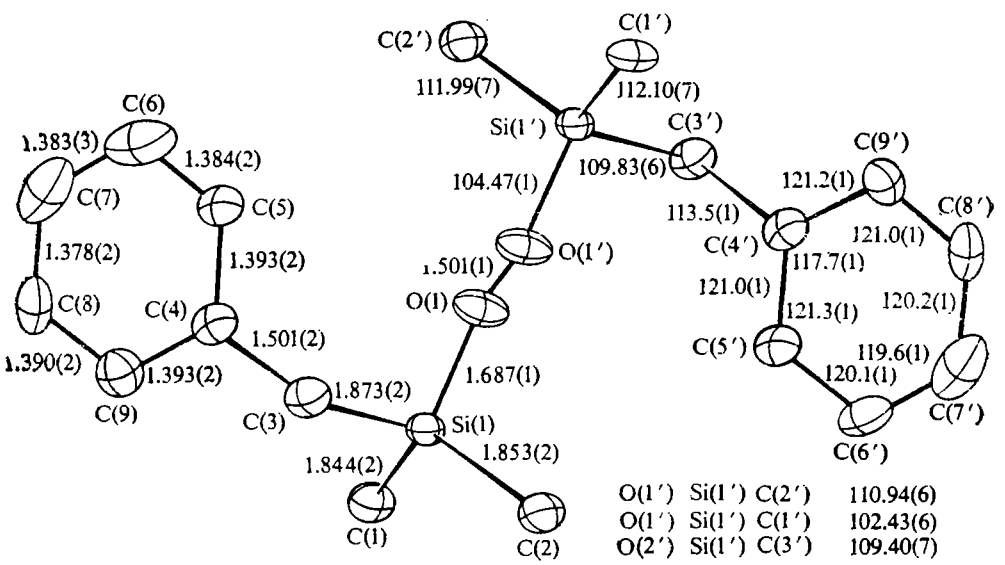


Figure 16. Structure of molecule XLI (C_i symmetry) [47].

Table 4 compares the geometrical parameters of organosilicon peroxides. Hexamethylcyclotrisilperoxide (XLV, Fig. 15) has the approximate D_3 symmetry. The most important characteristic of peroxide

Table 4. Geometrical Parameters of the SiOOSi and the OSiC Moieties Coplanar with It in Organosilicon Peroxides; Geometrical Parameters of Corresponding COOC and OCC Moieties in Three Related Organic Peroxides (d—O—O bond length, Å; τ—SiOOSi torsion angle, °; r—Si—O bond length; α—SiOO angle; ω— torsion angle round the O—Si bond in the OOSiC moiety; β—decreased OSiC bond angle in this moiety)

Compound	Formula	d	τ	r	α	ω	β	References
XL	$[(p\text{-}ClC_6H_4)Me_2SiO]_2$	1.498(2)	180	1.691 (1)	105.48(9)	178.5	100.88(8)	[46]
XLI	$[(C_6H_5CH_2)Me_2SiO]_2$	1.501(1)	180	1.687 (1)	104.47(6)	179.1	102.43(6)	[47]
XLII	$(Ph_3SiO)_2$	1.500(5)	180	1.668 (6)	103.6(5)	180	99.7(4)	[48]
XLIII*	$Ph_3SiOOGePh_3$	1.489(5)	180	1.472 (5)	104.4(4)	180	100.4(3)	[49]
XLIV	$(Me_3SiO)_2$	1.481(8)	143(6)	1.681 (3)	107(1)	156(3)	**	[50]
XLV	$(Me_2SiOO)_3$	1.492(2)	135.6(1)	1.674 (1)	104.9(1)	176.6***	102.4(1)	[51]
XLVI	$(Me_3CO)_2$	1.480	166(2)	1.460 (9)	104(1)	170(2)	**	[50]
XLVII	$(Ph_3CO)_2$	1.479(1)	180	1.459 (2)	107.7(1)	177.3	99.5(1)	[52]
XLVIII	$(Me_2COO)_3$	1.483(4)	135.6(3)	1.422 (5)	107.4(3)	178.8****	102.9(4)	[53]
XLIX	$[(tert\text{-}BuOO)_3Si]_2O$ C atom	1.477(8)	138	1.454 (5)	106(2)	175(2)	101(1)	[32]
	Si atom	1.477(8)	138	1.640 (8)	108(1)	174(1)	105(1)	

* The Si and Ge atoms statistically substitute one another; therefore the r, α, ω, and β values are average values of the parameters for an "average" (Si + Ge)/2 atom.
** The β values are not given in Ref. [50].
*** The O(2)O(1)Si(1)C(1) torsion angle (Fig. 15) in the molecules with an approximate D_3 symmetry.
**** The O(3)O(4)C(7)C(9) torsion angle; the approximate D_3 symmetry.

geometry is the torsion angle τ around the —O—O— peroxide bond. In XLV, the τ value (135.6°) is in keeping with the requirement that the peroxide groups form a closed cyclic system, as displayed by the coincidence of the τ values of XLV and its carbon analogue XLVI.

In bis(dimethylbenzylsilyl)peroxide (XLI, Fig. 16), as in other symmetric peroxides with bulky substituents (Table 4), $\tau = 180°$ and

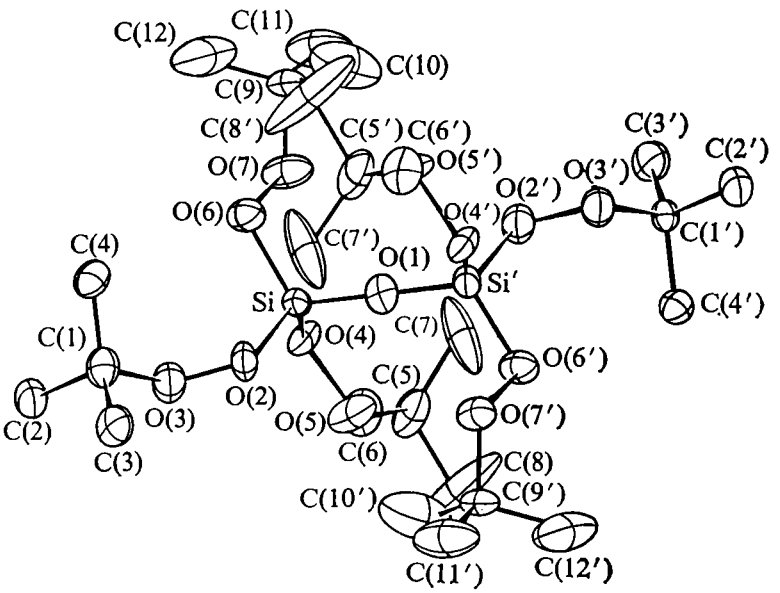


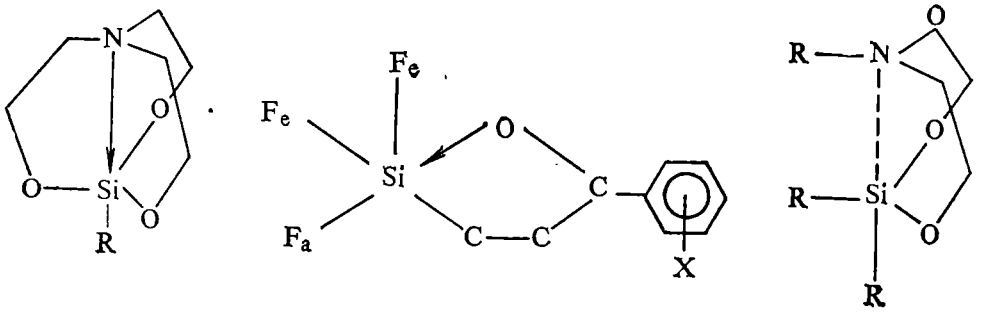
Figure 17. Structure of molecule XXIX (C_i symmetry) [32].

the molecule is centrosymmetric. Force field calculations confirm the advantage of a transoid centrosymmetric structure with $\tau = 180°$ for organosilicon peroxides [54, 55].

Organosilicon peroxides are characterized by the presence of planar transoid OOSiC moieties (their number is equal to that of peroxide groups) at each silicon atom and by 5-10° decrease of the tetrahedral OSiC angle in these moieties. In the molecule XIV there are two moieties of this sort at each Si atom and in the molecule XLI, one moiety (C(1)Si(1)O(1)O(1′)). Finally, in the molecule of hexakis-*tert*-butylperoxydisiloxane XXIX (Fig. 17), three planar OSiOO moieties are present at each Si atom and one moiety, at each of the tertiary carbon atoms.

6. DERIVATIVES OF PENTACOORDINATED SILICON

The most thoroughly structurally studied compounds of pentacoordinated silicon are silatranes [56-59], (aroyloxymethyl)trifluorosilanes [60-62], and 1,3-dioxa-6-aza-2-silacyclooctanes [63]:



The Si atom in these molecules, as in molecules of other derivatives of pentacoordinated silicon (see e.g. [64]), has a distorted trigonal bipyramidal geometry.

6.1. Silatranes

The molecular geometry of silatranes is discussed on the basis of silatranes with Me substituents at β-carbons and onium derivatives of 1-methylsilatrane.

The geometry of the coordination polyhedron of the Si atom in $ClCH_2Si[OCH(CH_3)CH_2)_2 \cdot (OCH_2CH_2)]N$ [56] and in the $RSi(OCH(CH_3)CH_2)_3N$ series where R = H (XLVIII), F (XLIX), $—CH_2Cl$ (L), and $—CH=CH_2$ (LI) is only slightly different from that observed in silatranes unsubstituted in the atrane framework, e.g. in $C_6H_5COOCH_2Si(OCH_2CH_2)_3N$ (LII) [59]. The presence of Me groups in positions 3, 7, and 10 of the silatrane framework does not exert a significant effect on the Si ← N interaction. The length of the Si ← N bond in XLII-LII is 2.12(1), 2.14(1), 2.146(3), 2.15(7), and 2.122(7) Å, respectively.

In the series of onium derivatives of 1-methylsilatrane, $[RCH_2Si(OCH_2CH_2)_3N]^+I^-$ (R = Me_2S^+ (LIII) (Fig. 18) [59], Me_3N^+ (LIV), and Ph_3P^+ (LV) [60]), the length of the transannular Si ← N bond correlates with an electron-acceptor character of the substituent R and is equal to 2.046(2) Å (LIII), 2.08(1) Å (LIV), and 2.07, and 2.12(1) Å (LV, two independent molecules). The N→ Si—C group is, as usual with silatranes, in fact linear, the NSiC angle being 179.1(1), 175.7(4), and 178.6 and 178.0(4)°, respectively. Intramolecular steric repulsion between the silatrane framework and the substituent R is observed only in LIV; the SiCR bond angles are 114.4(1), 121.2(9), and 113.6 and 115.3(6)°, respectively. The difference in the geometry of the cations in LV crystal is

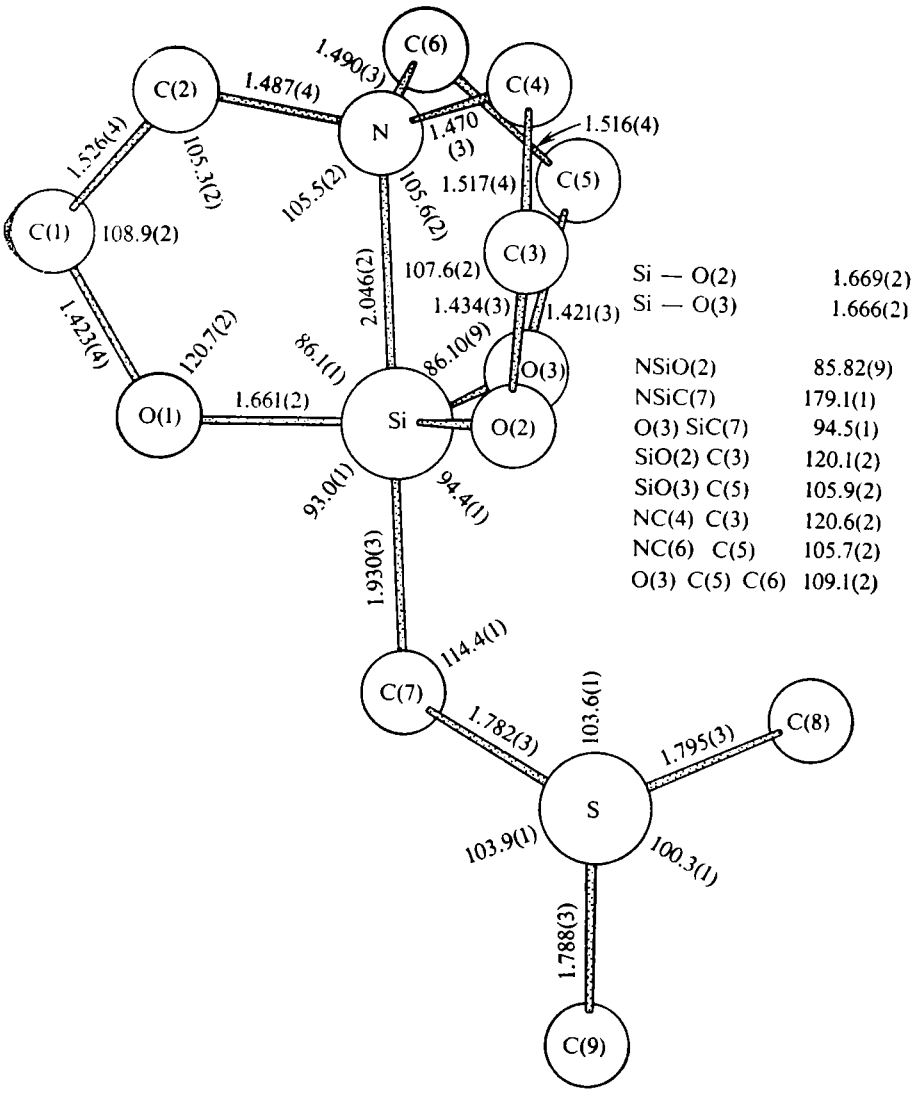


Figure 18. Structure of molecule LIII with bond angles [59].

explained by the different orientation of the C—Si ← N vectors with respect to the layers of I^- anions. The results of X-ray diffraction analysis of other silatranes are discussed in a recent review [67].

6.2. (Aroyloxymethyl)trifluorosilanes

The length of the Si ← O coordination bond in (aroyloxymethyl)trifluorosilanes LVI (X = 4-H), LVII (X = 4-F, Fig. 19), LVIII (X = 4-Cl), LIX (X = 4-Br), and LX (X = 2-Cl) [60-62] varies from 1.95(2) to 2.08(2) Å, and is independent explicitly of the position and nature of the substituent X. The elongation of the axial Si—F bond by abt. 0.03 Å, i.e. to 1.59(2)-1.61(1) Å, agrees with a

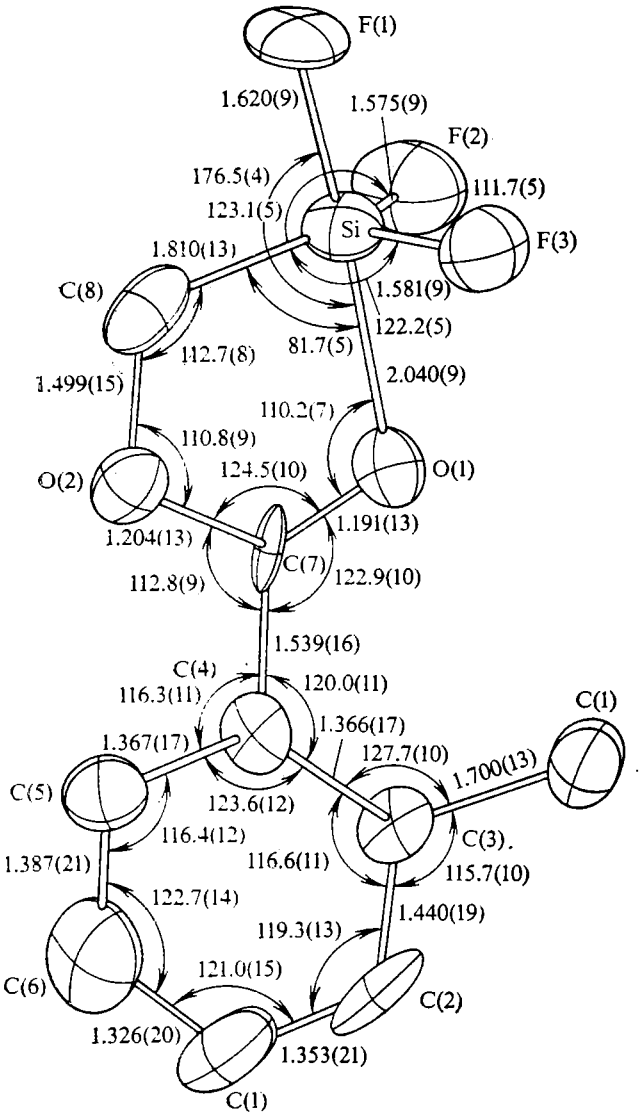


Figure 19. Structure of molecule LVII [62].

concept of the three-centre hypervalent F—Si—O bond. The Cl atom in LX (in position 2 of the aromatic ring) increases the angle between the planes of the 5- and 6-membered cycles to 17.5° [60].

6.3. 1,3-Dioxa-6-aza-2-silacyclooctanes and Other Derivatives of Pentacoordinated Silicon

Depending on the electronic and steric properties of substituents at the Si and N atoms in molecules of 1,3-dioxa-6-aza-2-silacyclooctanes, the Si...N distance increases from 2.30 Å when R = Ph, R′ = H (transannular Ni → Si interaction present) to 3.19 Å when R = Me, R′ = Ph (not present). The tetrahedral geom-

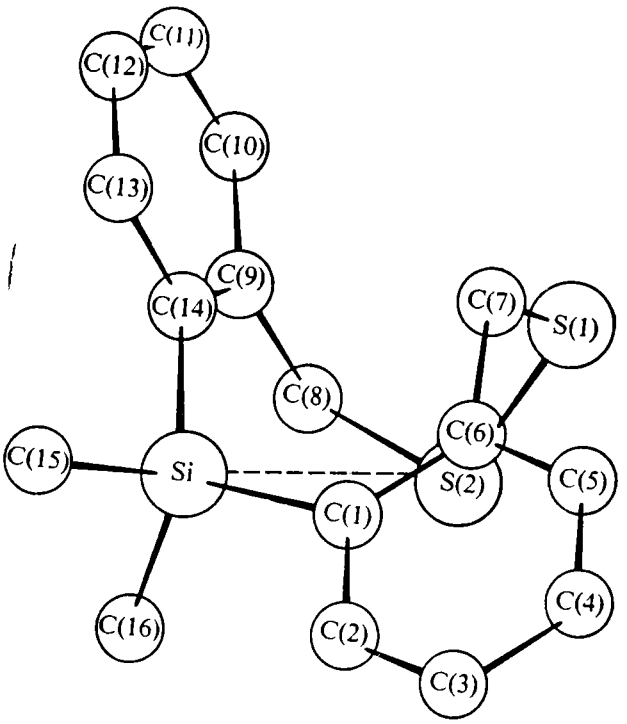


Figure 20. Structure of molecule LXI with transannular Si ← S(2) interaction [65].

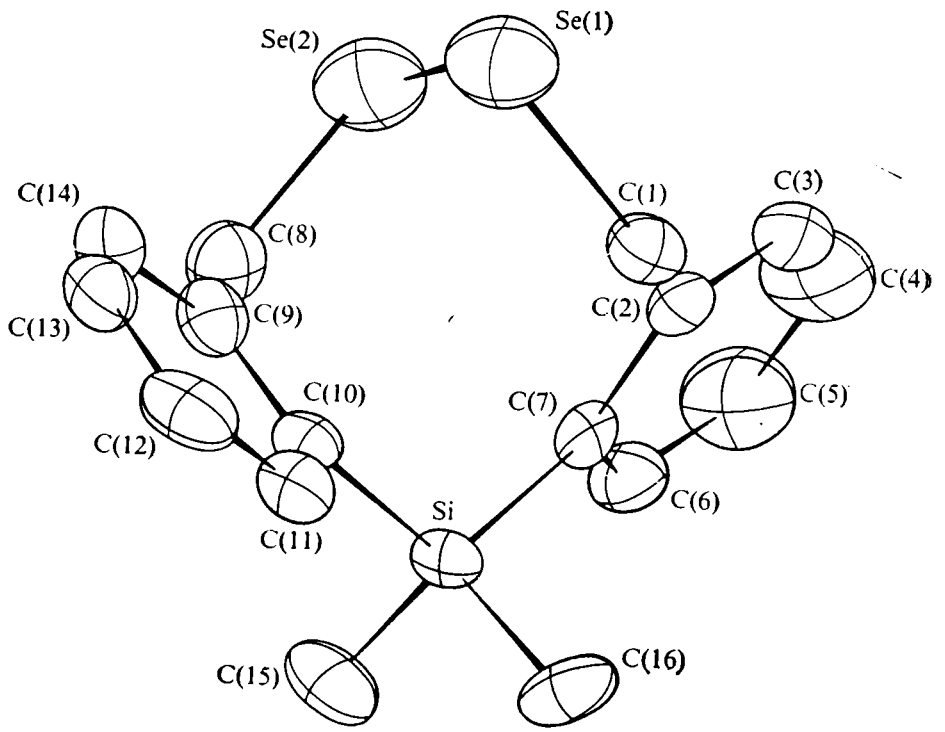


Figure 21. Structure of molecule LXII [66].

etry of the Si atom is being restored as the Si...N distance increases [63].

Intramolecular transannular Si...S interaction was first found in LXI (Fig. 20) [65]. A corresponding Si...S(2) distance (3.438(3) Å) is noticeably smaller than the sum of the van der Waals radii of Si and S (3.90 Å) or the "second" intramolecular Si...S(1) distance (4.190(3) Å). The Si...S(2) interaction is confirmed by a specific trigonal bipyramidal distortion of the coordination of the Si atom. Since the BB conformation of the 9-membered cycle of LXI is different from a corresponding conformation of the Se analogue, LXII (Fig. 21) [66], where both Si...Se distances are identical (4.322 and 4.328(2) Å), transannular Si ←Se interaction is precluded.

7. CONCLUSION

Data discussed in this short review do not exhaust the range of X-ray studies conducted by the authors. The papers cited are restricted by OSC simulating moieties of polyorganylsiloxanes, new OSC related to siloxanes, and OSC with higher coordination of the Si atom.

One can foresee a retention of interest in these important areas as well as in such domains of OSC structural chemistry as their reaction mechanism and pathways, relation between OSC structure and biological activity, structures of compounds with multiple bonds at the Si atom, and the nature of chemical bonds formed by the Si atom.

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2 Spectroscopic Study of the Donor-acceptor Properties of Silicon-containing Groups

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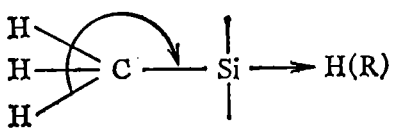
1. INTRODUCTION

In our systematic PMR, IR and UV spectroscopic studies of organometallic compounds much attention is paid to organic derivatives of silicon. Organosilicon compounds can be considered as model substances that simulate organic compounds of the IVB group elements and also as a subject of physical organometallic chemistry as a whole. Silicon-containing fragments possess both donor and acceptor properties with respect to molecular groups bound to them. This paper is aimed at analyzing the main factors determining the donor-acceptor properties of silicon-containing fragments in the ground and excited electronic states of molecules containing such fragments. Only those of our studies conducted at the Institute of Chemistry, USSR Academy of Sciences, that seem to be most important in view of the task set forth above, are reviewed here.

2. INDUCTIVE EFFECT OF SILICON-CONTAINING GROUPS

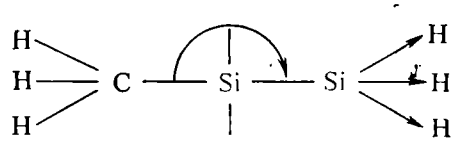
The silicon atom is less electronegative than the carbon atom. For this reason, the SiR_3 groups are more electron-donating or less electron-withdrawing than isostructural carbon-containing CR_3 fragments. For instance, at R = alkyl the trialkylsilyl groups are strong donors in relation to the inductive effect. This is expressed in large negative values of their Taft constants, σ^*. According to IR spectral data, σ^* for the $Si(CH_3)_3$ and $Si(C_2H_5)_3$ groups are -0.9 and -1.1, respectively [1], against -0.3 for $C(CH_3)_3$ [2]. The separation of the silyl group from the second fragment of the molecule by two methylene groups levels off the difference in the inductive effect of silicon-containing and isostructural organic radicals. For instance, σ^* of the $CH_2CH_2Si(CH_3)_3$ group (-0.2) [2] is close to the σ^* value of alkyl C_4-C_6 radicals (abt. -0.15). The values of the inductive constants of silyl substituents obtained by spectral methods sometimes vary noticeably, depending on the functional group linked to them [3-8]. This, on the one hand, requires caution in using the σ^* values found in the literature and, on the other hand, indicates the presence of non-inductive interactions in organosilicon com-

pounds, the interactions not peculiar to or only slightly expressed in carbon compounds. Hyperconjugation exemplifies these interactions in systems which, by analogy with isostructural organic compounds, should have featured substantial prevalence of the inductive effect. Hyperconjugation (σ, σ and σ, π conjugation) plays a more important part in organometallic compounds than in organic substances (see, for instance, Ref. [3]); among other things, this is related to a stronger polarizability of bonds formed by heteroelements. An important characteristic of hyperconjugation (as is the case with conjugation in general) is its enhancement resulting from the increasing difference of donor-acceptor properties of conjugated bonds. This characteristic of hyperconjugation is reflected in the IR [4] and PMR [5] spectra of SiR_4 and $HSiR_3$ (R = alkyl); the induction effect of R prevails in these compounds, whereas σ, σ conjugation,

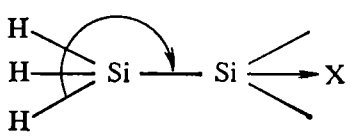


is not strong.

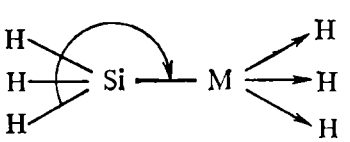
In R_3SiX (X is an electron-acceptor substituent), σ, σ conjugation is enhanced [4-6]. In disilane derivatives containing a highly polarizable Si—Si bond, σ* of the SiH_3 groups calculated with no allowance made for hyperconjugation has anomalous values ranging between +1.5 and —1.5, which is due to the ability of the SiH_3 fragment to act as acceptor



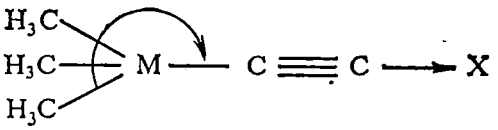
as well as donor



in σ, σ conjugation [7]. Hyperconjugation



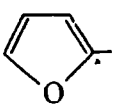
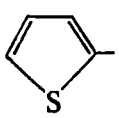
increases in going from M = Ge to M = Sn. Similarly,



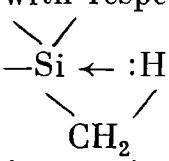
hyperconjugation grows with an increase in the atomic number of element M (in a Si < Ge < Sn series) and with the enhancement of the electron-acceptor properties of substituent X [8]. If these variable contributions of hyperconjugation are not taken into account, the calculation of the reliable σ^* values of the $M(CH_3)_3$ substituents is impossible. Among all resonance effects acting in the compounds of the IVB group, σ,σ conjugation, at least for silicon compounds, is not dominant. The resonance π acceptor effect of silyl substituents, traditionally explained by the participation in conjugation of vacant $3d$ orbitals of the silicon atom, is of more essential significance.

3. π ACCEPTOR PROPERTIES OF THE SiR_3 GROUPS

All spectroscopic and quantum-chemical studies (see, for example, the reviews [3], [9], and [10]) unambiguously testify to the existence (in addition to the inductive effect) of the resonance π acceptor effect of the SiR_3 groups with respect to substituents X bound to them and having unshared electron pairs or π electrons. In particular, the π acceptor properties of the SiR_3 groups are indicated by the following phenomena:

1. The impossibility of the interpretation of chemical shifts in the PMR spectra of the $-CH_3$, CH_3CH_2- [5, 11], $CH_2=CH-$ [12, 13],  [14],  [15, 16] groups in compounds with the CH_3-Si-X, CH_3CH_2-Si-X, $CH=CH-Si-X$ fragments (where X is any substituent with unshared electron pairs (*n* donor) or an α,β unsaturated hydrocarbon radical (π donor)), and also in furyl and thienyl derivatives only on the basis of the inductive effect of X. The acceptor properties of X, as predicted by the inductive mechanism, turn out to be less strongly expressed as a result of the oppositely directed *n* or π donor effect of X caused by the π acceptor properties of the silicon atom.

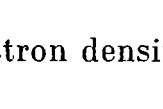
2. Lowered frequencies and elevated intensities of Si—H stretching modes in the IR spectra of $R_{3-n}X_nSiH$ and $R_{2-n}X_nSiH_2$ (X is a substituent of the *n* or π donor type), as compared with those expected if only the inductive effect of substituents X is considered [4, 6, 9, 10, 17-26]. Stretching vibrations ν(Si—H) are highly character-

istic in their shape. Mechanical interactions of the ν(Si—H) vibrations with other vibrations in the molecule are exceptionally weak. Therefore, the main reason for the changes in the frequency and intensity of the ν(Si—H) stretching modes is the influence of electronic effects of three substituents at the silicon atom. The frequency and intensity of the ν(Si—H) stretching modes in the IR spectra are distinguished by high sensitivity to this influence, which makes ample opportunities for studying both the inductive and the resonance effect of substituents bonded to the silicon atom. The ν(Si—H) frequencies were first studied in the IR spectra of compounds containing alkyl groups or the $(CH_2)_nX$ fragments at the silicon atom; here the *n* or π donor centre of X is not bonded by a direct chemical bond to the silicon atom. The substituents of this type possess, together with the inductive effect, weakly expressed resonance properties. To the latter belong σ, σ conjugation and intramolecular coordination between the silicon atoms and X (π donor); this gives rise to resonance donor properties expressed by the $(CH_2)_nX$ fragment. It has already been mentioned that the effect of σ, σ conjugation is not large under the conditions characterized by only a slight difference of the donor-acceptor properties of conjugated bonds (the case under discussion). For this reason σ, σ conjugation does not exert any significant influence on ν(Si—H) in molecules of the R_3SiH type where R is an alkyl group or an $X(CH_2)_n$ substituent, which is a weak acceptor with respect to the inductive effect. Intramolecular coordination  donor-acceptor interaction with the enthalpy of the formation of the coordination bond being of the order of several kJ/mol. Because of this, at about 300 K there exist as a rule both coordinated and intramolecular coordination-free molecules giving two bands in the region of stretching vibrations of the Si—H bond in the IR spectrum. An analysis of the IR spectra unequivocally attributes these bands to the free and coordinated forms*. Also, intramolecular coordination can easily be destroyed even by slightly electron-donor solvents (e.g. CCl_4). For this reason, molecules free of intramolecular coordination prevail in CCl_4 solutions; this fact (with the similarity of the absorption coefficients of ν(Si—H) in both forms taken into account) also favours the detection of the IR bands corresponding to free and coordinated molecules since the ν(Si—H) band of coordination-free molecules is more intense.

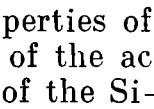
Thus, neither σ, σ conjugation nor intramolecular coordination in R_3SiH molecules (R is an alkyl or the $X(CH_2)_n$ group) have a deter-

* See however [66] and [68].—(*Ed.*)

mining effect on ν(Si—H), the dominating part being played by the inductive effect. For this reason, the ν(Si—H) frequencies in the IR spectra of such compounds are related to the sums of Taft's induction constants, $\Sigma\sigma^*$, by linear equations. R_3SiH and R_2SiH_2 give separate correlation lines parallel to one another: $\nu_I = 23\Sigma\sigma^* + 2112$ (R_3SiH), $\nu_I = 23\Sigma\sigma^* + 2121$ (R_2SiH_2). The existence of two correlation lines is apparently due to σ,σ conjugation. If a molecule of the type under consideration contains n or π donor substituents bonded to the silicon atom, the experimental values of ν_{exp} (Si—H) prove to be lower than those of ν_I(Si—H) calculated from these equations under the assumption that ν(Si—H) depends only on the inductive effect of the substituents. The differences, $\Delta\nu = \nu_I - \nu_{exp}$, are positive in all cases. The existence of $\Delta\nu$ is due to the π acceptor properties manifested by the silicon atom. The inductive I-effect of substituent X and the π acceptor effect of the silicon atom on substituent X act in opposite directions. The



transfer of electron density in the H—Si—X fragment (caused by the



π acceptor properties of the silicon atom) from X to Si results in the weakening of the acceptor properties of X, the decrease of the force constant of the Si—H bond, the decrease of ν(Si—H), and in the existence of the $\Delta\nu$ differences which are a quantitative characteristic of the π acceptor properties of the silicon atom. Together with the discussed influence of the π acceptor properties of the silicon atom on the energy of the Si—H bond, this resonance effect also brings about changes in the polarity of the Si—H bonds. A higher electronegativity of the hydrogen atom than that of the silicon atom results in polarization of the $Si^{\delta+}$—$H^{\delta-}$ bond which is reverse to that of the $C^{\delta-}$—$H^{\delta+}$ bond; in other words, the H atom bonded to the silicon acquires hydride properties. The polarity of the Si—H bond depends on the nature of substituents bonded to the silicon atom (donor substituents raise the polarity of the bond and acceptor substituents lower it). If the substituents feature an exclusively donor effect on the silicon atom, then because of a highly characteristic nature of the ν(Si—H) vibrations, the $A_I^{1/2} = 1.20 - 0.21\Sigma\sigma^*$ relationship holds true where A is the integrated intensity of the ν(Si—H) band. The $A^{1/2}$ value is linearly related to the dipole moment of the Si—H bond characterizing its polarity. This relationship is justified for isolated vibrations including the highly characteristic ν(Si—H) vibration when the Si—H bond can be effectively approximated by a diatomic molecule. If a molecule has n or π donor substituents bonded to the silicon atom, the experimentally measured $A_{exp}^{1/2}$ values turn out to be higher than $A_I^{1/2}$ calculated from this equation taking into account only the inductive effect

of the substituents at the silicon atom on the intensity of the ν(Si—H) bands. The differences $\Delta A^{1/2} = A_{exp}^{1/2} - A_I^{1/2}$ quantitatively characterize the resonance π acceptor effect of the silicon atom with respect to substituent X. Indeed, the transfer of electron density from

X to Si in the H—Si—X fragment due to the π acceptor properties of

the silicon atom leads to the emergence of a δ^- charge at the silicon atom. However, this charge is transferred from the silicon atom to a more electronegative hydrogen atom, thus slightly raising the polarity of the $Si^{\delta+}—H^{\delta-}$ bond. So, the inductive mechanism is responsible for the drop in the polarity of the Si—H bond as a result of the action of an *n* or π donor substituent, and the resonance mechanism (due to π acceptor properties of the silicon atom) brings about the growth of polarity. On the whole, the electron density

transfer from X to Si in the H—Si—X fragment, induced by the

silicon atom featuring the π acceptor properties, diminishes the acceptor ability of X, increases the polarity of the Si—H bond and the intensity of the ν(Si—H) IR band. An analysis of the Δν and $\Delta A^{1/2}$ values, which quantitatively characterize the influence of the π acceptor properties of the Si atom with respect to substituent X on the strength and polarity of the Si—H bond, allows investigation of most subtle details of conjugation in the Si—X fragments.

3. Lowered electron-donor ability of organosilicon derivatives of benzene [27-30], naphthalene [31], furan [32-34], thiophene [33-36], ethylene [37, 38], and acetylene [8] as compared with their carbon analogues (in contrast to the situation expected on the basis only of the inductive effect) on the formation of a hydrogen bond with electron acceptors (ground electronic state, as is evidenced by IR spectroscopy) and charge transfer complexes with π and σ acceptors (as UV spectroscopy shows, the charge transfer state when a positive charge exists in the HOMO of the π type) by these compounds acting as π donors. The resonance π acceptor properties of organosilicon fragments with respect to the π system of substituents remain practically unchanged in the ground and in the charge transfer state [8, 28, 30, 32-34, 36, 38].

4. The insufficiency of inductive ideas alone for the interpretation of the effect of substituents (e.g. SiR_3 type) on the frequency of the bending vibrations of the $=CH_2$ group in the IR spectra of organosilicon derivatives of ethylene [2]. The location of the frequency is determined by joint influence of the inductive and resonance effect of the substituents, the SiR_3 groups being among them.

5. The dependence of the frequency of Si—C stretching modes in the IR spectra [39] and of chemical shifts in the PMR spectra [40]

of compounds of the $[(C_2H_5)_3Si]_nX$ type (n is the valence of X) both on the inductive and the resonance effect of substituents X (elements of the Vth-VIIth groups of the Periodic System).

6. Lower n-donor ability of compounds containing the Si—O, Si—O—Si, Si—C=O [41-45], and $[(C_2H_5)_3Si]_2X$ (X = O, S, Se) [46] fragments and increased acidity of the hydrogen atom in compounds with the Si—N—H fragments [47] on the formation of a hydrogen bond, as a manifestation of the π acceptor properties of organosilicon substituents [48].

7. Typically electron-acceptor character of the SiR_3 substituents with respect to the aromatic ring. This follows from the analysis of the frequencies of electron transitions in the UV spectra of various benzene derivatives including phenylsilane [49]. The resonance π acceptor properties of SiR_3 with respect to the π system are enhanced in the excited electronic state as compared with the ground or charge transfer state.

The results of our systematic studies as well as the analysis of published data make it possible to formulate a number of general rules governing conjugation effects in the Si—X fragments in which the silicon atom manifests π acceptor properties [9, 10]. In compounds containing one Si—X bond (X is an element of the Vth-VIIth groups) or the Si-Y-Si group (Y = O, S, Se), the capability of conjugation between the Si and X or Y atoms in each of the groups of the Periodic System decreases with an increase in the atomic number of elements X or Y, i.e. in the N > P, O > S > Se, F > Cl > Br > I series. The decrease in the capability of conjugation between the Si and X or Y atoms in each of the groups of the Periodic System when element X or Y goes from the second period to the third is the stronger the larger the number of the group to which X or Y belongs. Thus, in the case of derivatives of elements of the Vth, VIth, and VIIth groups, conjugation sharply drops even in going from N to P, from O to S and then to Se, and from F to Cl, Br, and I. These features of conjugation between Si and n donor (NR_2, YR where Y = O, S, Se; F, Cl, Br, I) or π donor (aryl, vinyl, ethinyl, etc.) derivatives reproduce the principal characteristics of p,π and π,π conjugation of these substituents with unsaturated organic groups such as the aromatic ring or the multiple bond. In the Hammett-Taft system, the resonance constants, σ_R, of substituents are the quantitative measure of conjugation of the substituents with unsaturated groups. The relative capability of substituents of conjugation with the silicon atom is also closely correlated with the resonance constants of these substituents. Thus, the mechanism of the resonance π acceptor effect of the silicon atom with respect to substituents X is formally similar to the effects of conjugation of substituents X with the aromatic ring or the multiple bond [18, 20]. Systematic studies of organogermanium compounds (e.g. [10]) have shown that the main charac-

teristics of the π acceptor effect of the Ge and Si atoms are identical, but the magnitude of the effect in germanium compounds is lower than in silicon derivatives. In compounds containing groups of the C_6H_5—Y—Si—, RCOOSi—types, a competition between two conjugation effects—π acceptor effect of the silicon atom and the p, π conjugation—leads at Y = O to the prevalence of energetically more advantageous p, π conjugation and at Y = S or NR to a practical absence (at least, in the ground electronic state) of π acceptor properties of the silicon atom. All said above refers to the case when the only (*n* or π donor) substituent is bonded to the silicon atom. When the silicon atom has two or three similar substituents, X, their influence on the overall conjugation effect is, as a rule, nonadditive. In this case, the magnitude of the conjugation effect is determined not only by the mesomeric effect of substituents X, i.e. their *n* or π donor properties (as in compounds with the only substituent X), but also by effective charge at the silicon atom depending both on the mesomeric and inductive effects of substituents X. An increase in the effective positive charge at the silicon atom leads to a linear growth of its conjugation degree with substituents X [6, 19, 24, 26]. The strength of weak Si—X π bonds formed through conjugation depends on the values of the overlap integrals of the orbitals of the interacting Si and X atoms. The group overlap integrals of SiX_2 and SiX_3 are related to the two-centre integrals of the Si—X bonds by a complex relation rather than being an additive sum of the two-centre integrals [50]. That is why the energetic evaluation of the overall conjugation effect in a molecule testifies to its non-additive enhancement during the growth of the number of substituents at the silicon atom [21]. Similar dependences but with a lower magnitude of the π acceptor effects and a less substantial increase in the conjugation degree accompanying the identical (with that in silicon compounds) rise of the value of the effective positive charge at the central atom are observed in organogermanium compounds [10].

If the silicon (germanium) atom has several different substituents, the σ, *p* conjugation effect is observed (e.g. [3]). This conjugation type plays an important part in compounds with the N—Si—Cl and O—Si—Cl fragments. The σ, p conjugation effect in dialkylaminosilanes containing the $R_2\ddot{N}-\overset{|}{\underset{|}{Si}}-H$ group is favoured by a very strong *n* donor effect of the R_2N substituent.

The experimental data available by now testify to the rightfulness of the interpretation of the π acceptor properties of groups of the SiR_3 type on the basis of the *nd* orbital hypothesis [10]. Indeed, the (*p-d*) π bonds are formed in the Si—X fragments when three necessary and sufficient conditions are met:

1. Substituent X should possess n or π donor properties. The participation of d orbitals should give rise to effects similar to those observed in conjugation of π bonds in carbon compounds.

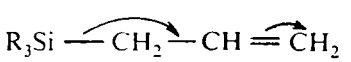
2. A positive effective charge should exist at the Si atom; an increase in the charge should be accompanied by the enhancement of the $(p\text{-}d)$ π bonds.

3. The overlap integrals of p_π and d_π orbitals of the interacting X and Si atoms should be large. This point is supported by the results of evaluations of the overlap integrals in a number of model systems [21].

These theoretical conclusions of the *nd* orbital hypothesis agree in full with the results of spectroscopic studies of the features of the π acceptor effects of the silicon atom discussed above. The possibility of a consistent and exhaustive interpretation of experimental data on the basis of the *nd* orbital hypothesis is an indirect support of a widespread opinion about the acceptor properties of the silicon and germanium atoms as the manifestation of the $(p\text{-}d)$ π interaction effect. On the other hand, the responsibility of *nd* orbitals for the acceptor properties of the elements of the silicon subgroup will be proved only as a result of thorough systematic quantum-chemical studies.

4. π DONOR PROPERTIES OF THE R_3SiCH_2 GROUPS

In the R_3SiCH_2X compounds where X is the aromatic ring or the multiple bond, the R_3SiCH_2 groups manifest in relation to X not only the inductive but also the resonance π donor effect (σ, π conjugation), e.g.



The π donor properties of the R_3SiCH_2 groups are indicated, among other things, by the following phenomena:

1. The insufficiency of the inductive ideas alone for the interpretation of the effect of the R_3MCH_2 substituents (M is an element of the silicon subgroup) on the frequency of the bending vibrations of $=CH_2$ in the IR spectra of corresponding allyl derivatives [2, 51] and on the chemical shifts in their PMR spectra ($X = CH{=}CH_2$) [51] and in the PMR spectra of furan derivatives ($X = 2\text{-}C_4H_3O$) [14].

2. Increased electron donor ability of the R_3SiCH_2 derivatives of benzene [27, 29, 52], furan [32], ethylene [30, 37], and acetylene [8] as compared with the level expected on the basis of the inductive effect of these substituents alone.

The shift of the $\nu(O-H)$ frequency of phenol in the IR spectrum

($\Delta\nu$) after the formation of hydrogen bond is a parameter characterizing the π donor properties in the ground electronic state (minor charge transfer from the π donor to the acceptor, phenol). The $\Delta\nu$ values show that the π donor properties of compounds containing the R_3MCH_2 substituents (M is an element of the silicon subgroup) at the donor centre are expressed stronger than in their carbon-containing analogues. This difference in electron donor ability cannot be explained by the dissimilarity of the electronegativity values of elements M. The growth of electron density at the π donor centre for larger atomic numbers of element M in a $Si < Ge < Sn$ series is a consequence of the growing role of the σ,π conjugation effect [3].

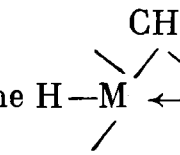
3. Increased π electron donor ability of the derivatives mentioned in Sec. 2 in the formation of π,π or π,σ charge transfer complexes with tetracyanoethylene or iodine (UV spectroscopy data) [8, 28-32, 38]. The main spectral parameter, i.e. charge transfer frequency, ν_{ct}, characterizes π donor properties in the charge transfer state when under the conditions of the experiment, as evidenced by the data of electron spectroscopy of CTC, an electron from the HOMO mostly localized at the aromatic ring or the double bond is almost completely (unlike the H complexes) transferred to the vacant orbital of the acceptor (tetracyanoethylene, iodine) and a positive charge is formed in the HOMO of the π donor. The presence of the charge may favour the enhancement of the conjugation of typically electron donor substituents of the +M type with the π donor centre. Indeed, the dependence between $\Delta\nu$ and ν_{ct} [28, 29] shows that the emergence of the positive charge at the aromatic ring in going from the ground state to the charge transfer state leads to an increase in the effects of π,π, p,π, and also σ,π conjugation of the substituent with the ring. On passing into the charge transfer state, benzyl derivatives of germanium manifest a larger enhancement of the σ,π conjugation than benzylsilanes [28, 29].

4. The impossibility of the interpretation of donor-acceptor properties of the R_3SiSiR_2 substituent at the aromatic ring or the double bond only on the basis of its inductive effect and π acceptor properties [3, 30, 38]. The $\Delta\nu$(OH) (spectroscopic basicity) and ν_{ct} (UV spectroscopy of CTC) values testify to less expressed donor properties of the R_3SiSiR_2 fragments with respect to π donor centres as against R_3SiCH_2. At first glance, this fact could have been interpreted as a result of a less intensely expressed σ,π conjugation in the case of disilyl derivatives. However, this is not the case. The R_3SiSiR_2 group combines the properties of the R_3Si and R_3SiCH_2 fragments in a peculiar manner participating in two oppositely directed resonance effects. First, this is the π acceptor effect of the silicon atom in the SiR_2 group. Second, this is the donor effect of the σ,π conjugation of the easily polarizable Si—Si bond with the aromatic ring.

The influence of the second effect dominates, and on the whole the R_3SiSiR_2 group is an electron donor. The less pronounced donor properties of R_3SiSiR_2 as against R_3SiCH_2 do not characterize the lower level of σ,π conjugation but express the participation of the R_3SiSiR_2 group in two oppositely directed resonance effects. If only the σ,π conjugation effect had acted, then the R_3SiSiR_2 group would have featured stronger donor properties than the R_3SiCH_2 fragment because of a higher polarizability of the Si—Si bond as compared with the Si—C bond.

An analysis of our results and of the published data [3, 10] shows that the π donor properties of the R_3SiCH_2 group (σ, π conjugation) in R_3SiCH_2X (X is a π donor substituent) become more pronounced with the manifestation of the donor properties of R and acceptor properties of X being stronger, and with the molecule passing from the ground state into the charge transfer state (for benzene derivatives). The R_3SiSiR_2 fragment exhibits more pronounced π donor properties as compared with R_3SiCH_2 [30]. The R_3MCH_2 groups (M = Ge, Sn) also feature π donor properties, the σ, π conjugation becoming stronger in a Si < Ge < Sn series (e.g. [3]). The profound analogy between conjugation of the π, π and p, π type and hyperconjugation (σ, π and σ, σ) in the compounds of elements from the silicon subgroup has been analyzed in our review [3].

5. *V* ACCEPTOR PROPERTIES OF THE SILICON ATOM

As was shown in the previous Section, the R_3SiCH_2 group in the R_3SiCH_2X compounds (X is the aromatic ring or the multiple bond) possesses resonance π donor properties with respect to X (σ, π conjugation). A different situation arises if X is an atom or a fragment with unshared electron pairs. In this case the non-inductive interaction between Si and X involves the transfer of electron density from X to Si (e.g. [53]), apparently because of intramolecular coordination with the participation of unshared electron pairs of X and vacant 3*d* orbitals of Si; however, other interaction mechanisms cannot be excluded [53]. IR spectroscopic studies have established lower degrees of manifestation of *n* donor properties by compounds of the R_3SiCH_2X type induced by the X groups (NR_2, OR, Cl) as a result of intramolecular coordination between Si and X in the fragments of the $SiCH_2X$ type and in groups of a more complex structure [54-58]. According to the IR spectroscopic data obtained for compounds with the  fragments (M = Si, Ge), the enthalpy

of formation of the coordination bond amounts to several kJ/mol [59]. Coordination is enhanced when the effective positive charge on the Si or Ge atoms grows and is partially or completely destroyed in donor solvents because of competition with the process of solvation of the M atom by the solvents [53-59]. The prevalence of the processes of specific solvation with the formation of the n, V and π, V complexes of donor-acceptor type between triethylsilane or -germane (V acceptors) and donor solvents (n and π donors) has been established by IR spectroscopy [60]. The V acceptor properties of compounds of the silicon subgroup become more pronounced with the atomic number of element M growing in the Si $<$ Ge $<$ Sn series, and for silicon derivatives are manifested to the lowest extent in the subgroup [53, 61]. The equilibrium constants of the complexing reaction become much higher at lower temperatures. Therefore a convenient method of examination of weak complexes is electronic emission spectroscopy of solutions frozen at 77 K [62, 63]. However, even in this case, when complexes are formed with compounds whose donor-acceptor properties are not strongly expressed (e.g. molecular oxygen [64]), phenylsilane derivatives mostly act as π donors (with π electrons of the aromatic ring involved). It seems at the same time that both π donor and V acceptor properties of phenylgermane derivatives are due to the participation of vacant $4d$ orbitals of the germanium atom. It is significant that the V acceptor properties of compounds of the silicon subgroup, in contrast to their π donor properties, strongly depend on the steric effects of substituents at the atom of element M [60, 64, 65].

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3 New Organic Compounds of Penta- and Hexacoordinate Silicon

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The search for new types of pentacoordinate silicon organic compounds and the investigation of their structure and properties are important problems of the organosilicon chemistry.

Studies in this field enable a better representation of the stereoelectronic structure and reactivity of silicon compounds with extended coordination numbers, which will provide a deeper understanding of the mechanism of nucleophilic substitution at the tetrahedral atom of the silicon subgroup elements. New penta- and hexacoordinate silicon compounds will without doubt include a number of substances very promising from the standpoint of synthesis and practical use.

We have carried out investigations in this direction for 20 years and have studied the structure, physical and chemical properties, and the biological activity of silatranes [1-4]. Recently the constancy of the total order of the hypervalent X—Si ← N bond in silatranes has been proved and new evidence for the effect of the medium on their structure and spectroscopic properties [5-12] has been obtained. We have also investigated complex formation of silatranes with protonodonors and weak Lewis acids [12-15], and outlined some trends for application of 1-iodosilatrane as a silatranizing agent [16, 17]. X-Ray diffraction of 3,7,10-trimethyl silatrane [18], an X-ray fluorescence analysis of Si-substituted silatranes [19, 20], and a detailed analysis of their vibrational spectra [21] have been carried out.

The investigations of the silatranes laid the foundation for the chemistry of pentacoordinate organosilicon derivatives. The results of our studies of the structure and stereodynamic behaviour of hitherto unknown pentacoordinate silicon derivatives containing the Si ← O coordinate bond are considered below.

The first compounds of this type were trimethylsilane C and Si-diacyloxy derivatives with a general formula $RC(O)OCH_2(CH_3)_2Si(O)COR'$ (I) in which the silicon atom pentacoordination was established by ^{29}Si NMR spectroscopy [22-24]. The efficiency of this method in determining the coordinate state of the silicon atom has been shown in studies of silatranes [25, 26] and their analogues [27, 28]. The extension of the silicon coordination

number results in the increase in its nuclear screening constant and consequently the upfield shift of the ^{29}Si NMR signal. The intramolecular interaction between the silicon atom and the oxygen atom of the carbonyl group in the acyloxymethyl fragment of molecule I takes place only when the Si-substituent electronegativity is fairly high (R = CF_3, but not CH_3).

Spectroscopic titration (^{29}Si NMR) of organylacyloxysilanes $XCH_2(CH_3)_{3-n}Si(OCOR)_n$ with trifluoroacetic CF_3COOM (R = CF_3, X = H or Cl; n = 2, 3; M = $HN(C_2H_5)_3$, $N(C_2H_5)_4$, or Na) or acetic salts CH_3COOM (R = CH_3; X = Cl, Br, or I; n = 3; M = $HN(C_2H_5)_3$) has for the first time revealed the existence of a new type of pentacoordinate silicon derivative, i.e. organyltetraacyloxysilicates $[XCH_2Si(OCOR)_4]^-M^+$ with R = CF_3, X = H (II) or Cl (III); R = CH_3, X = Cl (IV), Br (V), or I (VI), and dimethyltris(trifluoroacyloxy)silicate $[(CH_3)_2Si(OCOCF_3)_3]^-M^+$ (VII) [29]. The titration curve shape does not depend on the cation M. The $\Delta\delta^K = \delta^K - \delta^A$ values are determined by substituents on the silicon atom, and increase in absolute values as their total electronegativity increases.

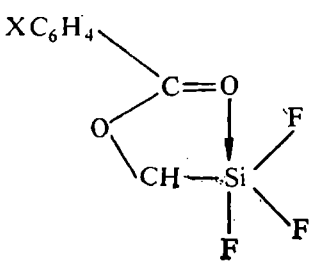
The stability of complex acyloxysilicates and therefore the complexing ability of the initial organylacyloxysilanes most likely grow in the order: VI < V < IV < VII < III $\leqslant$ II. Indeed, the ^{29}Si chemical shifts (δ_{Si}) in the spectra of II and III are independent of temperature. A temperature rise in acyloxysilicate solutions of IV-VII causes a downfield shift of the ^{29}Si resonance, and this probably reflects the shift of the equilibrium to the left:

$$XCH_2(CH_3)_{3-n}Si(OCOR)_n + RCOOM \rightleftarrows [XCH_2(CH_3)_{3-n}Si(OCOR)_{n+1}]^-M^+ \quad (1)$$

Trimethylacetoxysilane, dimethyl(halogenmethyl)acetoxysilanes, and trimethyl(trifluoroacetoxy)silane, in whose molecules the total electronegativity of substituents at the silicon atom is small, are entirely unable to form complex salts.

As evidenced by the ^{29}Si NMR data, pyridine forms a 2 : 1 complex with $CH_3Si(OCOCF_3)_3$, whereas the stronger base HMPTA (hexamethylphosphorotriamide) forms a 1 : 1 complex.

The best studied class of pentacoordinate silicon organic derivatives having the Si $\leftarrow$ O bond are (aroyloxymethyl)trifluorosilanes



(VIII)

Their synthesis was described for the first time in 1979 [30, 31]. According to X-ray diffraction the silicon atom in VIII displays a trigonal bipyramidal structure (X = H, 4-F, 2-Cl, 4-Cl, 4-Br) [32-34]. The oxygen atom of the carbonyl group occupies the axial position, where the Si ← O bond length amounts to 1.94-2.08 Å, which is 1.5 to 1.7 Å less than the sum of the Van der Waals radii of the Si and O atoms. The C—Cl and C=O bonds in the molecule VIII with X = 2-Cl are *cis*-oriented. The torsional angle between the planes of the carboxyl group and the benzene ring is between 7° and 17° [34].

The existence of the Si ← O intramolecular bond in compounds VIII is clearly seen in their IR-spectra [31, 35, 36]. In the crystalline state of VIII the carbonyl group stretching vibration, ν(C=O), is observed as an intense band at 1620-1640 cm^{-1}, i.e. it is shifted down about 100 cm^{-1} to the low-frequency region with respect to its position in benzoic esters [37]. In melts and weakly basic solvents the ν(C=O) bands of VIII are singlets and retain relatively low values of maxima frequencies. In the spectrum, apart from the main ν(C=O) band at 1660-1710 cm^{-1}, a peak near 1750 cm^{-1} appears and becomes predominant at higher temperatures. The spectral changes with temperature are reversible. Assuming that the first band corresponds to the coordinated carbonyl group, while the second band is due to the coordination-free one, we have established from the temperature dependence of the intensities of these bands the thermodynamic parameters of Si ← O bond dissociation:

$$4\text{-}FC_6H_4COOCH_2SiF_3 \rightleftharpoons 4\text{-}FC_6H_4COOCH_2SiF_3 \qquad (2)$$

These values are: $\Delta H = 8.1 \pm 0.7$ kcal/mol and $\Delta S = 15.3 \pm 0.8$ e.u. The Si ← O coordination significantly increases the C—O—C symmetric and antisymmetric vibration frequencies (1135 cm^{-1} and 1350 cm^{-1} respectively). This is caused by strengthening of the p, π-conjugation of the lone electron pair of the etheric oxygen with the carbonyl group polarized under the influence of the Si ← O bond. The $\nu_s(SiF_3)$ and $\nu_{as}(SiF_3)$ bands in alkyltrifluorosilane spectra are observed at 890 and 990 cm^{-1}. In molecules VIII, the natural coordinates of the axial and equatorial groups should not be mixed. These equatorial Si—F and Si—C stretching vibrations are probably mixed (ν_s = 870-875 cm^{-1} and ν_{as} = 965-975 cm^{-1}). In the IR-spectra of VIII in the condensed phase the band with a maximum at 810-825 cm^{-1} corresponds to $\nu(Si—F_a)$. The most important feature of the IR-spectra of VIII is the extremely high sensitivity of the ν(C=O) frequency (as well as the stretching vibration frequency of the second axial $\nu(Si—F_a)$ bond) to the solvent. In the Buckingham equation [38] the corresponding correlations for

VIII with X = H are

$$\nu(C{=}O) = 1688 - 99(\varepsilon - 1)/(2\varepsilon + 1) - 25(n^2 - 1)/(2n^2 + 1) \quad (3)$$
$$r = 0.996, \quad S_0 = 1.1$$

$$\nu(Si{-}F_a) = 836 - 109(\varepsilon - 1)/(2\varepsilon + 1) - 3(n^2 - 1)/(2n^2 + 1) \quad (4)$$
$$r = 0.999, \quad S_0 = 0.6$$

where ε is the dielectric constant and n is the refractive index of the medium. The first terms in Eqs. (3) and (4) practically coincide with the experimental values of $\nu(C{=}O)$ and $\nu(Si{-}F_a)$ for the gas phase of VIII. Therefore, the increase of the ε and n values reduces the orders of the C=O and Si—F_a bonds, thereby reflecting the substantial increase in the Si ← O coordination. The increase in the π- and σ-donor properties of the X substituent causes exactly the same qualitative changes.

The silicon atom pentacoordination in the molecules VIII is supported by NMR spectroscopy [39-41]. The ^{29}Si screening in VIII is 19-25 ppm higher than that in a model derivative of tetracoordinate silicon $ClCH_2SiF_3$ and is quite sensitive to the substituent X distant from the silicon atom:

$$\delta_{Si} = -94.9 + 5.168\sigma_p, \quad r = 0.999, \quad S_0 = 0.058, \quad n = 7 \quad (5)$$

Meanwhile, the influence of the substituents X on the δ_{Si} values of the model compounds $4\text{-}XC_6H_4COOCH_2Si(OR)_3$ with a tetracoordinate silicon atom, is poorly expressed and has a reverse tendency typical for tetrahedral molecules $RSiX_3$ (X is a highly electronegative substituent). Thus, the NMR and IR-spectroscopy evidence demonstrates that the influence of the substituent X on the silicon atom in molecules VIII is transmitted not only through the π- and σ-bonds. The electron effect of the substituent X determines the nucleophilic ability of the carbonyl oxygen atom and consequently the degree of intramolecular interaction.

The ^{19}F NMR spectra of VIII solutions in CH_2Cl_2 above 200 K contain an average (owing to rapid pseudorotation of the trigonal bipyramidal silicon atom) resonance ^{19}F NMR signal of axial and equatorial fluorine atoms. The silicon pentacoordination in VIII molecules is evident only from the considerable downfield shift of the ^{19}F resonance and the smaller absolute value of spin-spin coupling constants ^{29}Si-^{19}F as compared with the $ClCH_2SiF_3$ spectra.

Non-equivalence of the axial and equatorial fluorine atoms is observed in the ^{19}F NMR spectra of VIII solutions below 150 K. The spin-spin coupling constants between F_a and F_e are typical for pentacoordinate silicon derivatives (45-50 Hz). The free energy of activation of the process of pseudorotation of a Si atom at the coalescence temperature of the ^{19}F NMR signals confirms that the stereodynamic stability of molecules VIII and consequently the degree of

Si ← O intramolecular interaction increase with increasing electrodonor property of the substituent X.

The chemical shifts of the axial fluorine atom, unlike those of the equatorial ones, are sensitive to the substituent X

$$\delta(F_a) = -127.43 - 2.23\sigma_p \quad r = 0.961, \quad S_0 = 0.206, \quad n = 7 \tag{6}$$

This reflects the predominant *trans*-effect of substituents on the pentacoordinate silicon atom.

As evidenced by ^{13}C and ^{17}O NMR, the screening of the carbon atom in the C=O group of VIII is 8 ppm smaller, while that of the C_1 and C_4 atoms in the aromatic ring and the oxygen atom in the carbonyl group are 6 ppm, 2 ppm, and 60 ppm*, respectively, greater than in $XC_6H_4COOCH_2Si(OR)_3$. This difference is due to the electron density transfer in the molecule VIII from the aromatic fragment to the carbonyl group and the Si atom.

The ^{13}C and ^{17}O NMR chemical shifts of the C=O group and the C_1 atom are related to the inductive and resonance constants of the substituent X, i.e.

$$\delta(^{13}C{=}O) = 175.3 - 2.8\sigma_1 - 1.0\sigma_p^- \tag{7}$$

$$r = 0.974, \quad S_0 = 0.2, \quad n = 7$$

$$\delta(^{13}C_1) = 124.4 + 5.8\sigma_1 + 10.2\sigma_p^+ \tag{8}$$

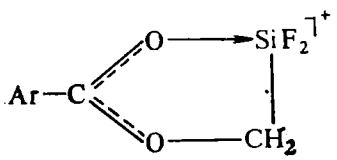
$$r = 0.993, \quad S_0 = 0.5, \quad n = 7$$

$$\delta(^{17}O) = 277.3 + 28.0\sigma_p \tag{9}$$

$$r = 0.97, \quad S_0 = 2.7$$

The non-specific interaction with the solvent and the temperatures of VIII solutions do not affect much the NMR spectral parameters (^{13}C, ^{19}F (averaged) and ^{29}Si). The increase in the temperature of solutions or the diminishing of the solvent polarity causes the spectral changes consistent with the lower Si ← O interaction; the stronger the Si ← O bond, the less it is influenced by external factors.

Intramolecular Si ← O coordination is responsible for high dipole moments (5-7 D) and specific electron-impact fragmentation of compounds VIII [31, 58]. In most cases, the molecular ion fragmentation involves abstraction of the fluorine atom to form a stable cation of the suggested structure:

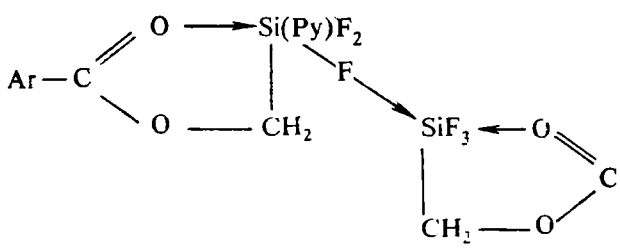


When organic bases such as pyridine, trimethylamine, and dimethylsulfoxide are added to solutions of VIII in non-polar media, in-

* Relative to $XC_6H_4COOCH_2CF_3$ [41]

soluble 1 : 1 adducts precipitate [42]. The ν(C=O) frequencies at 1640-1660 cm^{-1} in the IR-spectra indicate that the intramolecular Si←O bond remains unchanged in the complexes. The intense bands at 680-710 and 750 cm^{-1} arisen from hexacoordinate silicon compounds [43], correspond to the ν(Si—F) vibrations. The change in the slope of straight lines produced by dielcometric titration of VIII with pyridine in CH_2Cl_2 is clearly defined when the component ratio is 2 : 1 and is less clear in a ratio of 1 : 2. The second bent is most likely to correspond to an adduct with a hexacoordinate silicon with no Si ← O bond. The 2 : 1 ratio confirms the formation of a complex with an unusual composition. In benzene the complex remains in solution and is prevailing because the 1 : 1 adduct precipitates.

In the IR-spectra of the 2 : 1 complexes of VIII with pyridine in CH_2Cl_2 only one ν(C=O) band with a frequency indicative of retention of the intramolecular Si ← O bond is observed. The intensity of the ν(Si—F) bands corresponding to the pentacoordinate silicon derivative is lower than those measured for VIII in CH_2Cl_2. The bands corresponding to Si—F bonds in hexacoordinate silicon occur between 680 and 710 cm^{-1} and near 750 cm^{-1}. The above data probably point to the existence of an equilibrium



(10)

between molecule VIII (pentacoordinate silicon atom) and complexes including two molecules with a hexacoordinate silicon, and one pyridine molecule.

If the 1 : 2 complexes prevail in CH_2Cl_2, the ν(C=O) bands of free carbonyl groups at 1690-1720 cm^{-1} and the ν(Si—F) bands corresponding to the hexacoordinate silicon species are observed in the IR-spectrum.

The 1 : 2 complexes are predominant in solutions of VIII in pyridine. When even small amounts of pyridine are added to the solution of VIII in acetonitrile, a free carbonyl group band appears in the IR-spectrum.

According to NMR data [39] the ^{29}Si screening of VIII in dimethylsulfoxide and hexamethylphosphorotriamide is 40 to 50 ppm higher than that in non-basic solvents. The spectroscopic (^1H NMR) titration of these compounds with HMPTA confirms the formation of 1 : 1 and 2 : 1 complexes: In the 1 : 1 complexes the intramolecular Si ← O bond is likely to be retained, whereas in the 2 : 1 complexes it is evidently absent.

Therefore, the composition and structure of VIII-organic base complexes depend on the component ratio in solution, the medium properties, and the base type. The equilibrium transitions between molecules VIII and their complexes in solution are accompanied by extension of the silicon coordination number from 5 to 6.

In methyl(aroyloxymethyl)fluorosilane molecules, $XC_6H_4COOCH_2Si(CH_3)_nF_{3-n}$, the increase in the number of methyl groups attached to the silicon atom substantially reduces the coordination ability of silicon atom. Unlike VIII the compounds of this type with $n = 1$ (IX) and $n = 2$ (X) are liquids with the coordinate and non-coordinate forms in equilibrium. This is also the case for solutions of IX and X in inert and weakly basic organic solvents [35, 44]. In the IR-spectra this dynamic equilibrium is revealed as a doubling of the ν(Si—F), ν(C—O—C), and ν(C=O) vibration bands [45]. The latter make it possible to determine the thermodynamic characteristics of the dissociation of intramolecular IX and X complexes (see Table 1) and to establish the effect of the medium on the Si ← O bond state [35, 44].

Table 1. Thermodynamic Parameters of Dissociation of Intramolecular Si ← O bond of Compounds $(CH_3)_n(XC_6H_4COOCH_2)SiF_{3-n}$ (ΔH, kcal/mol, ΔS, e.u.)

Medium	X = H, $n = 1$			X = 4-CH_3, $n = 1$			X = H, $n = 2$		
	ΔH	ΔS	K_{298}	ΔH	ΔS	K_{298}	ΔH	ΔS	K_{298}
Gas	2.8	6.1	0.18	2.2	4.6	0.23	1.3	3.9	0.72
n-$C_{10}H_{22}$	3.0	6.6	0.16	2.2	4.9	0.27	1.3	4.6	1.07
$(n\text{-}C_4H_9)_2O$	3.0	7.3	0.24	2.1	5.1	0.34	0.9	3.9	1.41
CH_3CN	3.0	8.0	0.32	2.1	5.1	0.38	0.9	6.6	5.76

The table and the corresponding data for VIII [31] demonstrate that the intramolecular coordination strength is reduced in the order VIII > IX > X. The independence of the experimental ΔH of IX and X from the medium properties has been established. This is not due to the constant strength and length of the Si ← O bond but is probably caused by self-consistency of bonds (the Si ← O and —O—C= bonds, for example, invariably become stronger as the Si—F_a and —C=O bonds weaken).

The increase in the dissociation constant of the intramolecular complexes, K_{298}, with increasing ε of the medium is caused by higher ΔS. The role of the entropy term is particularly important with low ΔH values.

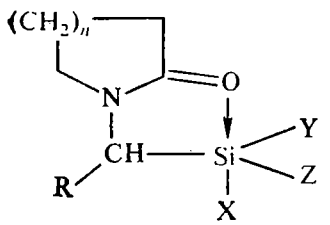
An analysis of the Buckingham type equations (3) and (4) for IX and X shows that the ν(C=O) frequency of the coordinate carbonyl group is more sensitive to ε and n of the medium as compared with the coordination-free group. The results obtained indicate that the medium effect on the interaction within the C=O ← Si—F_a fragment in molecules VIII-X enhances as the strength of the Si ← O bond increases.

The IR-spectra of the compounds $XC_6H_4COO(CH_2)_nSiF_3$ with $n = 2$ and 3 display the significance of the steric and entropic control for the Si ← O intramolecular coordination. The derivatives with $n = 3$ do not contain the Si ← O bonds in any medium [31]. The compounds with $n = 2$ in non-polar solvents at 160-420 K exist as an equilibrium mixture of both the coordinate and non-coordinate forms. Even at low temperatures the equilibrium is substantially shifted towards the latter (without the Si ← O bond) [46].

As evidenced by ^{29}Si and ^{19}F NMR [39], the degree of Si ← O intramolecular interaction in $RCOOCH_2SiF_3$, where R = CH_3, C_6H_5CH=CH, or 2-C_4H_3S, is approximately the same as in VIII. The ability of the Si atom to pentacoordination in thioanalogues of VIII (i.e. (aroylthiomethyl)trifluorosilanes, XI, and (acetylthiomethyl)trifluorosilane, XII) is considerably lower than that in VIII [47]. There are three ν(C=O) absorption bands in the IR-spectra of their solutions. Two high-frequency bands ν_1 and ν_2 probably correspond to free carbonyl groups of two rotational isomers. The third band, a low-frequency ν_3, is assigned to stretching vibrations of the coordinate carbonyl group. The effect of the solvent dielectric properties on the ν_3 value is thrice as large as that on ν_1 and ν_2, and is 1.5 times that observed for ν(C=O) of compounds VIII.

The existence of concentration relationships for the ratio of the ν_1, ν_2, and ν_3 band intensities, as well as the ν_3 frequency, indicates that contrary to compounds VIII, not only intra-, but also intermolecular Si ← O coordination is possible for XI and XII. The silicon atom pentacoordination in molecules XI and XII is supported by ^{19}F and ^{29}Si NMR evidence [48].

The intramolecular Si ← O bond also exists in the series of Si-substituted N-(silylmethyl)lactams (XIII), which contain at least one very electronegative substituent at the silicon atom [49-52]:

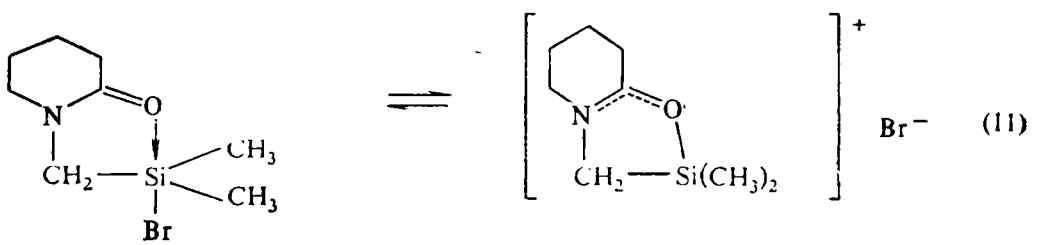


n = 1, 2, 3

R = H or CH_3

(XIII)

^{29}Si NMR evidence demonstrates that the degree of the Si ← O interaction in Si-substituted N-(dimethylsilylmethyl)lactams (Y = Z = CH_3, R = H) increases in the following order of the lactam cycle size change (provided the substituent X is the same): $5 \ll 7 \approx 6$. Within each series of lactam derivatives the Si ← O bond is the stronger, the higher the electronegativity of substituent X and the polarizability of the Si—X bond. When the temperature of solutions of the majority of these compounds drops, the screening constants of the silicon atom increase. This indicates a stronger intramolecular coordination and/or a higher equilibrium constant between the "acyclic" (containing no Si←O bond) and "cyclic" (containing Si ← O bond) forms. The inverse temperature dependence of the δ_{Si} of N-(dimethylbromosilylmethyl)valerolactam is most likely to be due to the equilibrium between the normal and the ionic species:



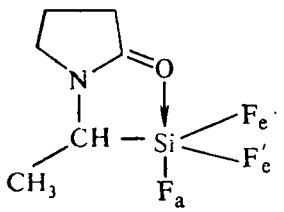
(II)

The strengthening of the Si ← O bond at low temperatures seems to promote dissociation of readily polarizable Si—Br bonds and to increase the concentration of the ionic form in solution.

The intramolecular Si ← O interaction affects the spectral characteristics of both the acceptor (Si) and donor (O) atoms in molecules XIII containing a pentacoordinate silicon atom. The electron density transfer through the Si ← O bond causes an upfield shift of the ^{17}O NMR signals relative to the model tetracoordinate silicon compounds $(RO)_mSi(CH_3)_{3-m}CH(R)\overline{NC(O)CH_2(CH_2)_nCH_2}$. This is caused by both polarization and lower order of the C=O bond. The Si ← O bond strengthening causes a downfield shift of carbonyl ^{13}C resonance. The NMR spectra of XIII show a linear relationship between the ^{13}C and ^{17}O chemical shifts of the carbonyl group which are induced by the intramolecular Si ← O interaction.

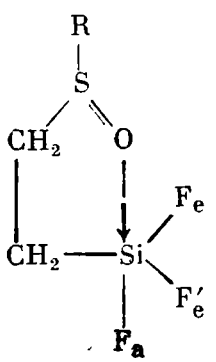
NMR spectroscopy gives some information on the stereodynamic behaviour of XIII containing an asymmetric endocyclic or asymmetric carbon atom either in or attached to the silicon atom. The ^{1}H NMR spectra of Si-substituted 4-phenyl-N-(dimethylsilylmethyl)pyrrolidone $X(CH_3)_2SiCH_2\overline{NC(O)CH_2CH(C_6H_5)CH_2}$ reveal (at 173 K) the anisochronyl of the equatorial methyl groups at the trigonal bipyramidal silicon atom. Dynamic NMR indicates that the pseudorotation barrier is about 11 kcal/mol.

Using N-(1′-trifluorosilylethyl)pyrrolidone



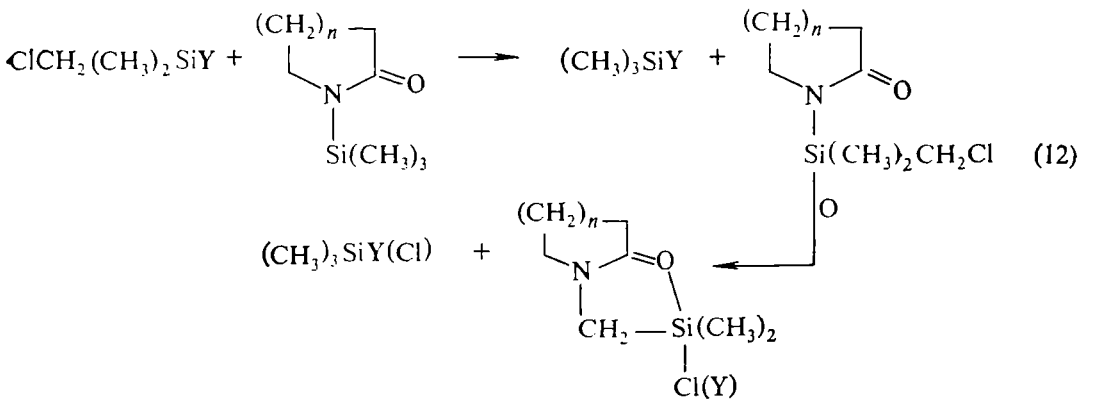
we were able to measure, for the first time, the spin-spin coupling constant between two equatorial fluorine atoms [51]. The ^{19}F NMR spectra of this compound at 173 K contain a triplet signal of the axial (F_a) fluorine nucleus and two doublets of the equatorial fluorine nuclei (F_e) doublets. The value of $^2J(F_eF_e')$ is 15 Hz which is considerably smaller than $^2J(F_aF_e) = 42$ Hz. The values of $^1J(SiF_e) = {}^1J(SiF_e') = 220$ Hz and $^1J(SiF_a) = 243$ Hz are typical for fluorine derivatives of pentacoordinate silicon. Diastereotopy of equatorial fluorine nuclei is caused by slow inversion of the pentacoordinate (owing to intramolecular Si ← O bonding) silicon atom and the asymmetry of the α-carbon atom attached to it. None of the above reasons *per se* can explain the non-equivalence of all the fluorine nuclei.

A similar non-equivalence of all the fluorine atoms occurs at low temperatures too in the NMR spectra of organyl(trifluorosilylethyl)-sulfoxides (XIV) [53]. This is due to the trigonal bipyramidal structure of the Si atom and the chirality of the S atom:



^1H and ^{29}Si NMR enabled us to elucidate the formation mechanism of Si-substituted N-(dimethylsilylmethyl)lactams when N-(trimethylsilyl)lactams are reacted with Si-functional derivatives of dimethyl (chloromethyl)silane $ClCH_2(CH_3)_2SiY$ [50]. The C—Cl bond in the latter is less reactive than the Si—Y bond. Nevertheless, it was assumed [54] that a similar reaction of acyclic silylamides with $XCH_2(CH_3)_2SiY$(X, Y = Cl, Br) involves C—X bond cleavage without participation of the Si—Y bond.

^{1}H NMR and ^{1}H-^{29}Si INDOR allowed us for the first time to identify the intermediate and final products of reaction

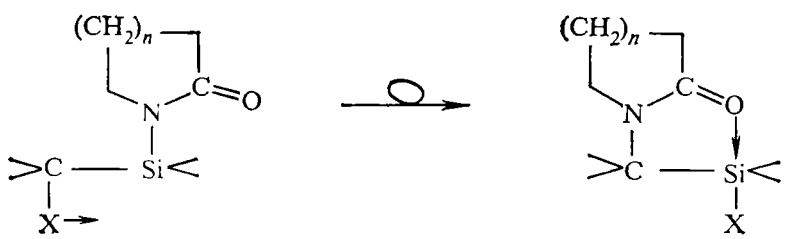


(12)

and to prove that the reaction proceeds via a rapid intermediate stage of *trans*-silylation with subsequent rearrangement.

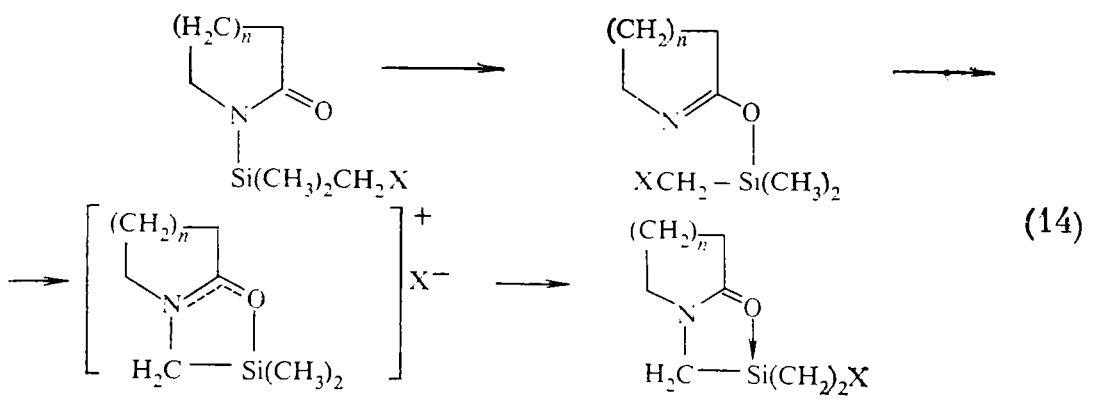
The degree of Si ← O interaction in the final product affects the rearrangement kinetics. For example, in the case of a six-membered lactam cycle ($n = 2$) the *trans*-silylation product exists only at temperatures below 190 K, whereas its five-membered lactam cycle ($n = 1$) analogue remains unchanged up to 293 K. In both cases the temperature rise causes the *trans*-silylation products to rearrange into the corresponding Si-substituted N-(dimethylsilylmethyl)lactam.

This rearrangement may be either via a direct diatropic conversion:



(13)

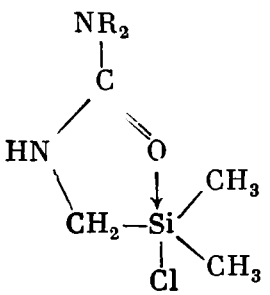
or via the O-tautomer form and N-alkylation:



(14)

Although rearrangements of the $XCH_2SiY \rightleftarrows YCH_2SiX$ type are not uncommon in the organosilicon chemistry, the second mechanism seems the more likely, since the formation of the coordinate Si ← O bond facilitates this rearrangement (especially when $n = 2$).

Similar conversions were found [55] for comparatively stable N-dimethyl(chloromethyl)silyl-N′,N′-(diorganyl) ureas. When allowed to stand for a long time in nitrobenzene or during distillation they rearrange into pentacoordinate silicon derivatives XV:



(XV)

Thus these investigations indicate that it is not uncommon for the coordination number of the silicon atom in organic compounds to extend under certain conditions. The Si atom must be bound by a readily polarizable bond to at least one highly electronegative substituent, with a five-membered ring closure being more advantageous for the intramolecular bonding than six-membered chelation. The formation of the intramolecular coordinate bond depends both on the steric factors and on the entropy change of the process. If the total electronegativity of the substituent at the silicon atom is sufficiently high, the substituent can transfer to the hexacoordinate state involving also the formation of mixed intra- and intermolecular complexes. The medium often strongly influences the degree of intramolecular coordination.

Most of the observed regularities governing the mutual effect of substituents at the pentacoordinate silicon atom and the effect of external factors on the structure of pentacoordinate silicon derivatives are best explained in terms of the theory of hypervalent bonds [2, 5, 56, 57]. The rearrangement of the $XCH_2SiY \rightleftarrows YCH_2SiX$ type is facilitated by the formation of intramolecular coordinate bonding in the final product.

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4 Organosilicon Compounds Containing a Multiply p_π-p_π Bonded Silicon Atom. First Evidence for Existence and Characterization of Silaalkenes ($R_2Si=CR_2$)

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1. INTRODUCTION

Until the mid-1960s all attempts to detect compounds having silicon multiply bonded to carbon, nitrogen, oxygen or other elements had failed. This led to the formulation of the so-called "classical double bond rule" [1, 2]. According to this rule silicon, like other elements with the principal quantum number greater than 2 should not be able to form double or triple p_π-p_π bonds, and organosilicon compounds having such bonds were considered nonexistent [3].

In 1967 we first proved the existence of a new structural class of organosilicon compounds, the silaalkenes ($R_2Si=CR_2$), and obtained the first characteristics thereof. The compounds referred to above are formed as unstable intermediates during the selective thermal [4 → 2 + 2]-cyclodecomposition of 1,1-dimethyl-1-silacyclobutane (DMSCB) (reaction 1) and other monosilacyclobutanes [4-11]. Further conversion of the 1,1-dimethyl-1-silaethylene (DMSE) intermediate proceeds as regioselective "head-to-tail" cyclodimerization to form 1,1,3,3-tetramethyl-1,3-disilacyclobutane (TMDSCB) (reaction 2).

$$\begin{array}{l} Me_2Si{-}CH_2 \\ \quad | \quad | \\ H_2C{-}CH_2 \end{array} \xrightarrow{>400\ ^\circ C} [Me_2Si=CH_2] + C_2H_4 \qquad (1)$$

$$2[Me_2Si{=}CH_2] \rightarrow \begin{array}{l} Me_2Si{-}CH_2 \\ \quad | \quad | \\ H_2C{-}SiMe_2 \end{array} \qquad (2)$$

Since the time of this discovery, there has been an ever growing interest among the researchers in the problem of formation of various multiple p_π-p_π bonds by silicon, such as Si=C, Si=N, Si=O, Si=Si, Si=P, Si=S, Si≡C, and Si≡N. This has been a subject of several reviews [12-23].

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* Now deceased.—(*Ed.*)

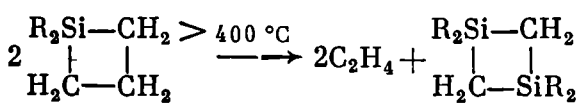
This paper presents a brief overview of our studies on the thermal decomposition reaction of monosilacyclobutanes that have made it possible to discover the previously unknown property of the Si^{IV} atom to form multiple p_π-p_π bonds with carbon and other elements. It also surveys some works bearing on the problem of p_π-p_π bonding of group IVB elements [4-11, 24-90].

A schematic representation of a set of studies that first permitted the characterization of silaalkenes as a new class of organosilicon compounds is shown in Fig. 1. Here, a key role is played by the thermal decomposition of monosilacyclobutanes (1), which substantiated the idea of silaalkenes' existence. In this reaction the intermediate silaalkenes (2) were identified by kinetic (1a), chemical (1b), and thermochemical (1c) methods and it was ascertained that instability of silaalkenes was not due to their unimolecular decomposition but their strong tendency towards bimolecular transformations, viz. cyclodimerization and other addition reactions to the Si=C double bond (3). Thus, it became clear what experimental conditions could ensure the isolation or stabilization of silaalkenes for their study outside the generation zone or upon cessation of the generation reaction (4). Indeed, the application of VLPP (4a) and matrix isolation (5) techniques in combination with both cryochemical (6) and spectroscopic (7) methods has not only provided support to the earlier chemical and kinetic evidence for the existence of silaalkenes but offered possibilities for gaining insight into their structure and the nature of the silicon-carbon double bond. Finally, identification of silaalkenes in the course of thermal decomposition of monosilacyclobutanes gave impetus to a large number of quantum-chemical studies (8) which demonstrated that the ground state of the silaalkenes' molecules involved a singlet with a closed shell, i.e. a true Si=C double bond exists.

Let us first consider the evidence obtained from the kinetic study of DMSCB thermal decomposition and pyrolysis of DMSCB in the presence of compounds that react with the silicon-carbon double bond. These two methods led for the first time to the identification of $Me_2Si{=}CH_2$ [8, 9].

2. KINETIC EVIDENCE FOR THE FORMATION OF 1,1-DIMETHYL-1-SILAETHYLENE UPON PYROLYSIS OF METHYL-SUBSTITUTED MONOSILACYCLOBUTANES

In preparative sense, pyrolysis of monosilacyclobutanes is their transformation into 1,3-disilacyclobutanes [4-6]:



(3)

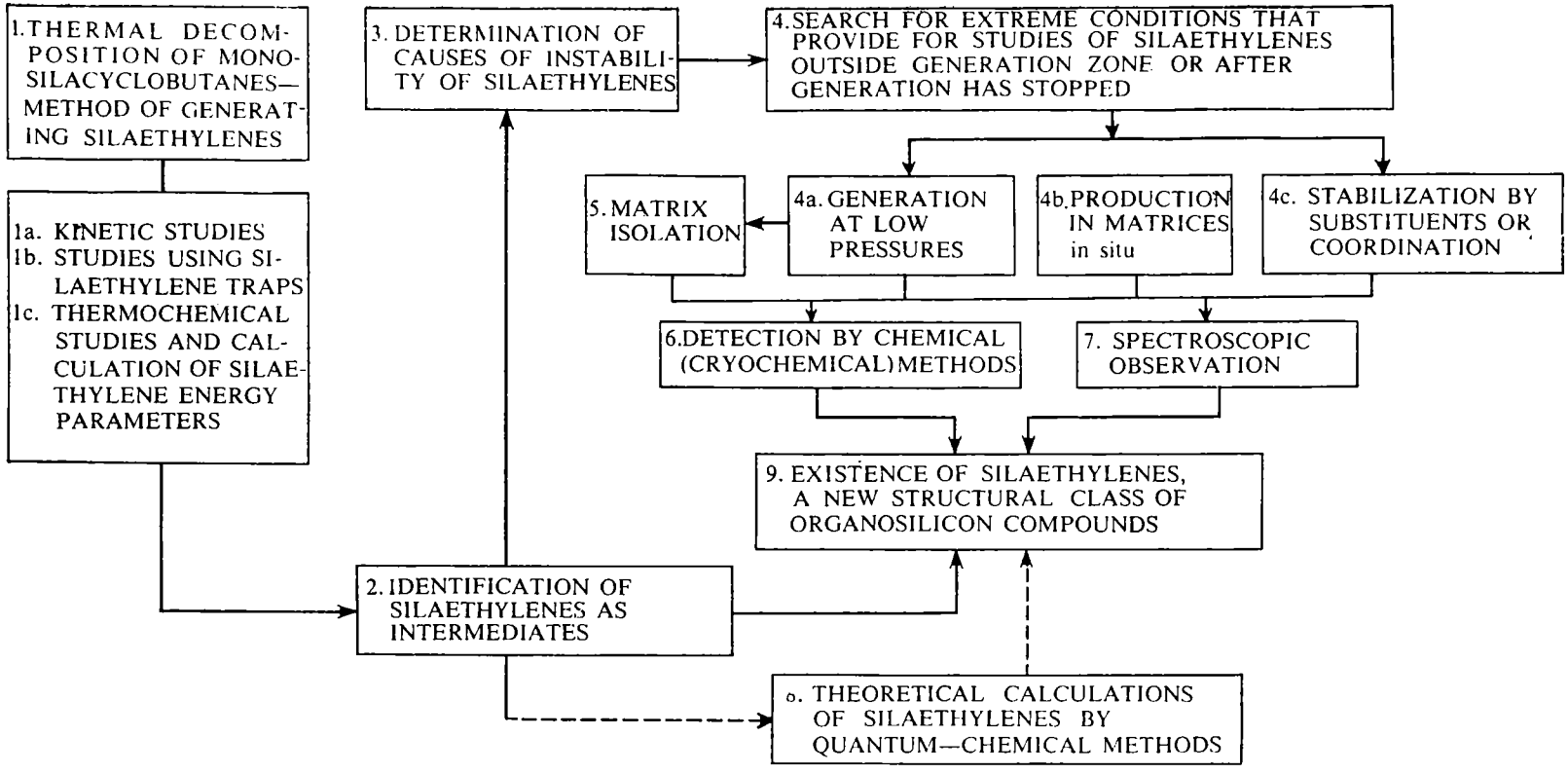
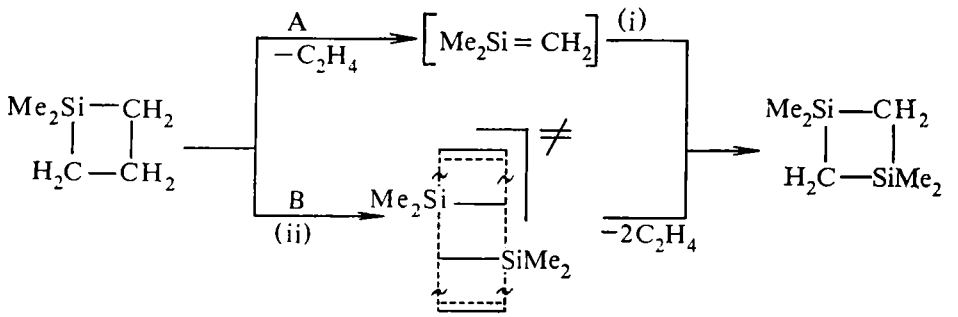

1. THERMAL DECOMPOSITION OF MONOSILACYCLOBUTANES—METHOD OF GENERATING SILAETHYLENES
1a. KINETIC STUDIES
1b. STUDIES USING SILAETHYLENE TRAPS
1c. THERMOCHEMICAL STUDIES AND CALCULATION OF SILAETHYLENE ENERGY PARAMETERS
2. IDENTIFICATION OF SILAETHYLENES AS INTERMEDIATES
3. DETERMINATION OF CAUSES OF INSTABILITY OF SILAETHYLENES
4. SEARCH FOR EXTREME CONDITIONS THAT PROVIDE FOR STUDIES OF SILAETHYLENES OUTSIDE GENERATION ZONE OR AFTER GENERATION HAS STOPPED
5. MATRIX ISOLATION
4a. GENERATION AT LOW PRESSURES
4b. PRODUCTION IN MATRICES in situ
4c. STABILIZATION BY SUBSTITUENTS OR COORDINATION
6. DETECTION BY CHEMICAL (CRYOCHEMICAL) METHODS
7. SPECTROSCOPIC OBSERVATION
8. THEORETICAL CALCULATIONS OF SILAETHYLENES BY QUANTUM—CHEMICAL METHODS
9. EXISTENCE OF SILAETHYLENES, A NEW STRUCTURAL CLASS OF ORGANOSILICON COMPOUNDS

Figure 1. Schematic representation of the studies that resulted in the discovery of silaalkenes.

For this process, two alternative mechanisms (see Scheme 1) were considered: unimolecular, involving reactions (1) and (2) (R=Me), and bimolecular:

Scheme 1



(i) $Me_2Si=CH_2$ (ii) DMSCB

The choice between the unimolecular mechanisms involving the silaalkene intermediacy (route A) and the bimolecular one involving no silaalkenes (route B) was made from kinetic studies [8, 9]. During pyrolysis in the static system (394.3-450.7 °C, 1.9-54.5 torr), the only products of the thermal decomposition of DMSCB were ethylene and TMDSCB in the ratio 2:1. At up to 50% conversion, the reaction obeys a first order kinetic equation, the rate constant (k_1) being independent of DMSCB initial pressure and the ratio of reactor surface to volume (that is, the process is homogeneous). The relationship between k_1 and temperature is governed by the equation

$$k_1(s^{-1}) = 10^{15.6\pm0.3}\exp(-62300 \pm 800/RT) \quad (4)$$

The higher the conversion and the accumulation of ethylene in the reactor, the greater the contribution of the slow reverse reaction of [2 + 2]-cycloaddition of ethylene to DMSE, reaction (1), which reduces the DMSCB decomposition rate. Studies of the effects of the added ethylene have revealed good agreement between the results obtained and those calculated:

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B + C$$

$$2B \xrightarrow{k_2} D$$

$$-\frac{d\ln A}{dt} = k_1\left\{1-\frac{k_{-1}}{(2k_1k_2)^{1/2}}\cdot\frac{C}{A^{1/2}}\left[1-\frac{k_{-1}}{2(2k_1k_2)^{1/2}}\cdot\frac{C}{A^{1/2}}\right]\right\} \quad (5)$$

where A = DMSCB, B = DMSE, C = C_2H_4, and D = TMDSCB.

Graphic solution of Eq. (5) has given the following Arrhenius relationship:

$$k_{-1}/k_2^{1/2}\ (\text{litre}^{1/2}\cdot\text{mol}^{-1/2}\cdot\text{s}^{-1/2}) = 10^{3.3\pm1.2}\ \exp\ (-14500 \pm 4000/RT) \tag{6}$$

whence $E_{(-1)} - 1/2E_{(2)} = 14.5 \pm 4$ kcal/mol

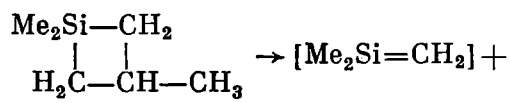
Later, investigating the kinetics of the pyrolysis of DMSCB by VLPP/cryochemistry [91] and VLPP/MS [54, 55] methods, we found E_2 to be equal or close to zero. Hence, $E_{(-1)} = 14.5 \pm 4$ kcal/mol. The enthalpy of reaction (1) is calculated as

$$\Delta H_1^\circ = E_{(1)} - E_{(-1)} \tag{7}$$

$$\Delta H_1^\circ = 47.8 \pm 4.8 \text{ kcal/mol}$$

Independent determination of ΔH_1° from the photoionization mass-spectrometric [43, 53] and photoelectron spectroscopic [92] data gives 43.8 kcal/mol, which corresponds to $E_{(-1)} = 18.5$ kcal/mol.

Pyrolysis of 1,1,3-trimethyl-1-silacyclobutane (1,1,3-TMSCB) also proceeds as [4 → 2 + 2]-cyclodecomposition to afford DMSE and propylene [29, 59]:



$$\rightarrow [Me_2Si{=}CH_2] + C_3H_6 \tag{8}$$

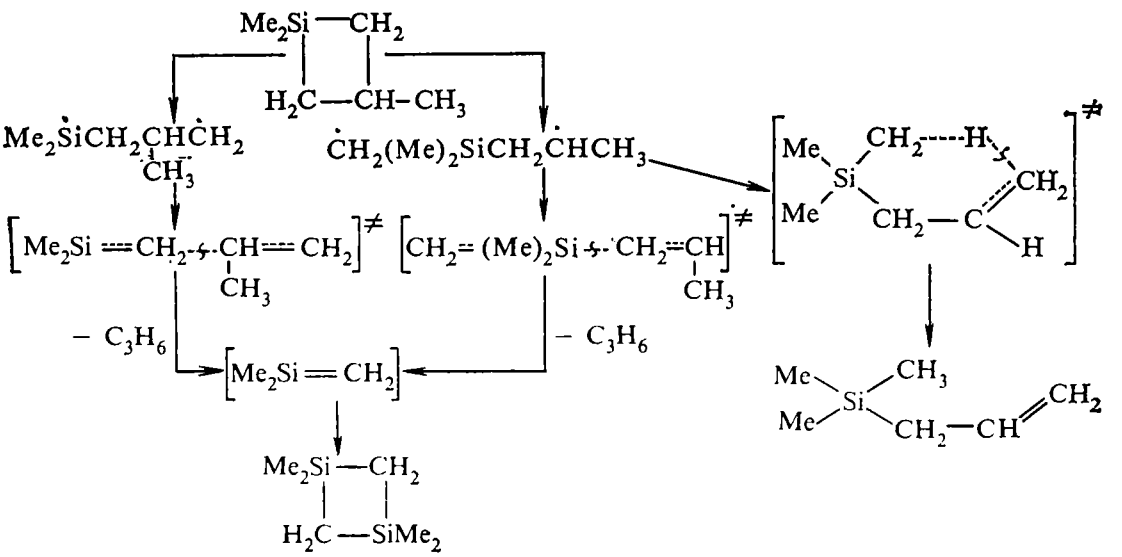
Unlike DMSCB, thermal decomposition is accompanied by slow isomerization of 1,1,3-TMSCB into allyltrimethylsilane (ATMS). This is especially interesting because, on the one hand, this reaction is the first example of isomerization of monosilacyclobutanes into alkenylsilanes, and, on the other hand, indicates that pyrolysis of monosilacyclobutanes starts with a homolytical rupture of the C—C bond in the four-membered ring. The Arrhenius relationships for the rate constants of decomposition (k_d) and isomerization (k_i) of 1,1,3-TMSCB are given by Eqs. (9) and (10):

$$k_d\ (\text{s}^{-1}) = 10^{16.3\pm0.3}\ \exp\ (-63200 \pm 950/RT) \tag{9}$$

$$k_i\ (\text{s}^{-1}) = 10^{15.6\pm0.3}\ \exp\ (-63240 \pm 780/RT) \tag{10}$$

It can be seen that both reactions exhibit similar activation energies but have different pre-exponential factors. For isomerization, the latter is less by about one order of magnitude than for decomposition. Scheme 2 illustrates decomposition and isomerization of 1,1,3-TMSCB in terms of the biradical mechanism recognized for cyclobutanes.

Scheme 2



It is seen that decomposition can be ascribed to the onset of the process involving cleavage of either the Si—C or the C—C bond in the four-membered ring, whereas isomerization, solely to the opening of the ring's C—C bond. The k_d to k_i ratio is independent of temperature. Therefore, the difference in the rates of these processes will be wholly determined by entropy restrictions, which seem to be more pronounced in the case of izomerization because this process involves formation by the radical $^{\cdot}CH_2Si(Me_2)\dot{C}H_2CHCH_3$ of a rigid six-membered cyclic transition state ($\Delta S_d^{\neq} - \Delta D_i^{\neq} = 3.1$ cal/deg·mol).

Isomerization into alkenylsilanes is presumably a common reaction of C-alkyl-substituted monosilacyclobutanes. Indeed, due to 1,5-migration of H-atom in the primary biradical $^{\cdot}CH_2Si(Me_2)CH(CH_3)\dot{C}H_2$ a similar isomer, vinyldimethylethylsilane, was formed together with the decomposition product upon pyrolysis of 1,1,2-trimethyl-1-silacyclobutane (1,1,2-TMSCB)[93]. A recent kinetic study on pyrolysis of 1-methyl-1-vinyl-1-silacyclobutane has again confirmed that cleavage of the C—C bond in the ring takes place preferably during gas-phase thermal decomposition of monosilacyclobutanes [94]. In this respect, the thermal decomposition of monosilacyclobutanes is in marked contrast to their liquid-phase polymerization which involves ring opening at the Si—C bond [14].

Thus, the kinetic evidence cited has first helped discarding a bimolecular mechanism for the thermal decomposition process of monosilacyclobutanes. Second, it furnished important evidence to that the first step of the two-step process involving reactions (1) and (2) is a homogeneous, unimolecular [4 → 2 + 2]-cyclodecomposition

of monosilacyclobutanes which yields two unsaturated molecules containing C=C and Si=C double bonds. This proceeds in accordance with Eqs. (1) and (8).

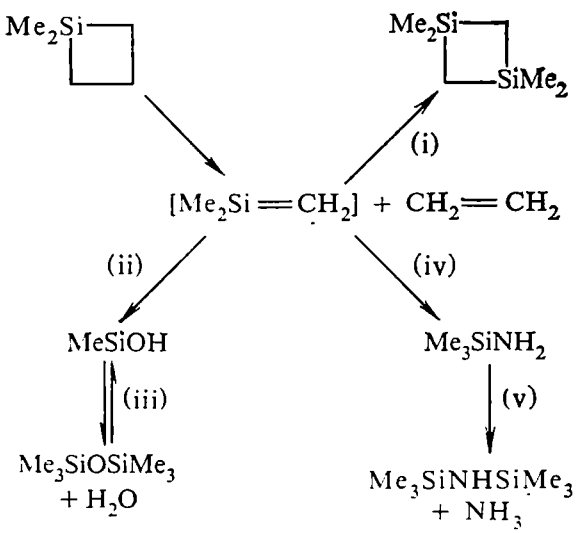
3. CHEMICAL EVIDENCE FOR THE FORMATION OF SILAALKENES DURING PYROLYSIS OF MONOSILACYCLOBUTANES

As is shown in Sec. 2, the first evidence for the existence of compounds containing a double-bonded silicon was obtained from kinetic studies [8, 9]. According to these the formation of 1,3-disilacyclobutanes during thermal decomposition of monosilacyclobutanes should follow a unimolecular mechanism, and involve steps for the generation and cyclodimerization of silaalkenes. To identify silaalkenes by chemical methods, we studied the pyrolysis of DMSCB in the presence of chemical traps. Using the traps capable of reacting with multiple bonds we succeeded in suppressing partially or completely cyclodimerization of intermediate silaalkenes. In each case we ascertained to what extent the structure of the adduct corresponded to the concepts of a silicon-carbon double p_π-p_π bond. Silaalkenes like olefins were found to add with molecules a labile hydrogen and undergo [2 + 2]- and [2 + 4]-cycloaddition. That is, they gave the adducts expected from silicon analogues of olefins. Because of the specificity of the double bond to silicon, silaalkenes are more reactive than olefins in addition reactions. The reaction of DMSE with water and ammonia [8, 9] was the first chemical evidence for the existence of intermediate silaalkenes in pyrolysis of monosilacyclobutanes. In the static system with an equimolar quantity of added water and in the flow system with higher concentrations of H_2O the formation of TMDSCB was completely suppressed to produce novel products, trimethylsilanol and hexamethyldisiloxane (Scheme 3). Similar results were obtained upon pyrolysis of DMSCB in the presence of added ammonia. However, only a condensation product, viz. hexamethyldisilazane was isolated because of the instability of the primary adduct.

Subsequently, formation of silaalkenes during pyrolysis of monosilacyclobutanes, was corroborated by the reactions involving addition of alcohols [47, 95], amines [95], hydrogen halides [91, 96], nitriles [97], chloro- and alkoxysilanes [98-100], and cyclosiloxanes [31, 101] to the Si=C double bond.

Another chemical evidence for the existence of silaalkenes was provided by [2+2]-cycloaddition reactions first deduced from the kinetic studies of thermal decomposition of DMSCB [8, 9]. These are cyclodimerization of DMSE and reactions of silaalkenes with ethylene and propylene. For example, due to [2+2]-cycloaddition

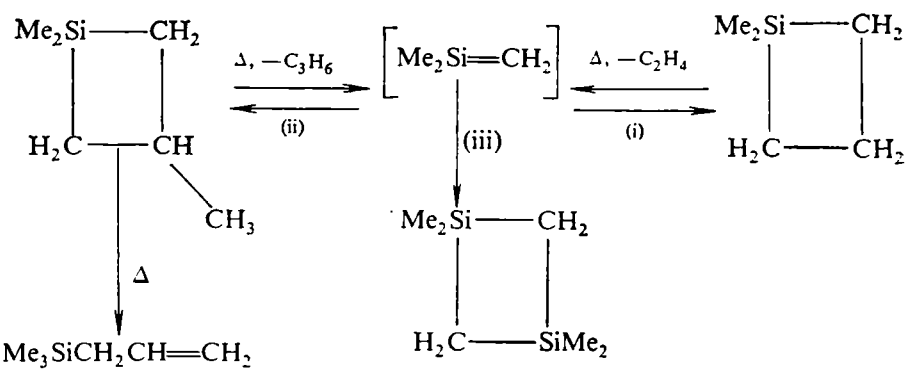
Scheme 3



(i) $Me_2Si{=}CH_2$, (ii) H_2O, (iii) Me_3SiOH, (iv) NH_3, (v) Me_3SiNH_2

of DMSE to propylene 1,1,3-TMSCB and its isomer, allyltrimethylsilane (Scheme 4)) [33, 34], are formed upon thermal generation of DMSE from DMSCB in the presence of excess propylene. Reactions with olefins proceed at a slower rate than cyclodimerization. For these [2 + 2]-cycloaddition reactions to compete with cyclodimerization, a large excess of olefin is required.

Scheme 4



(i) C_2H_4 (ii) C_3H_6 (iii) $Me_2Si{=}CH_2$

Silaalkenes thermally generated from monosilacyclobutanes are also involved in the [2 + 2]-cycloaddition reactions with carbonyl [15, 19, 95], thiocarbonyl [103], and azomethine [104] compounds as well as with alkynes [105], oxygen [96], and dimethylsilanthione [88, 90]. Thus, cogeneration of $Me_2Si{=}CH_2$ and $Me_2Si{=}S$ by copy-

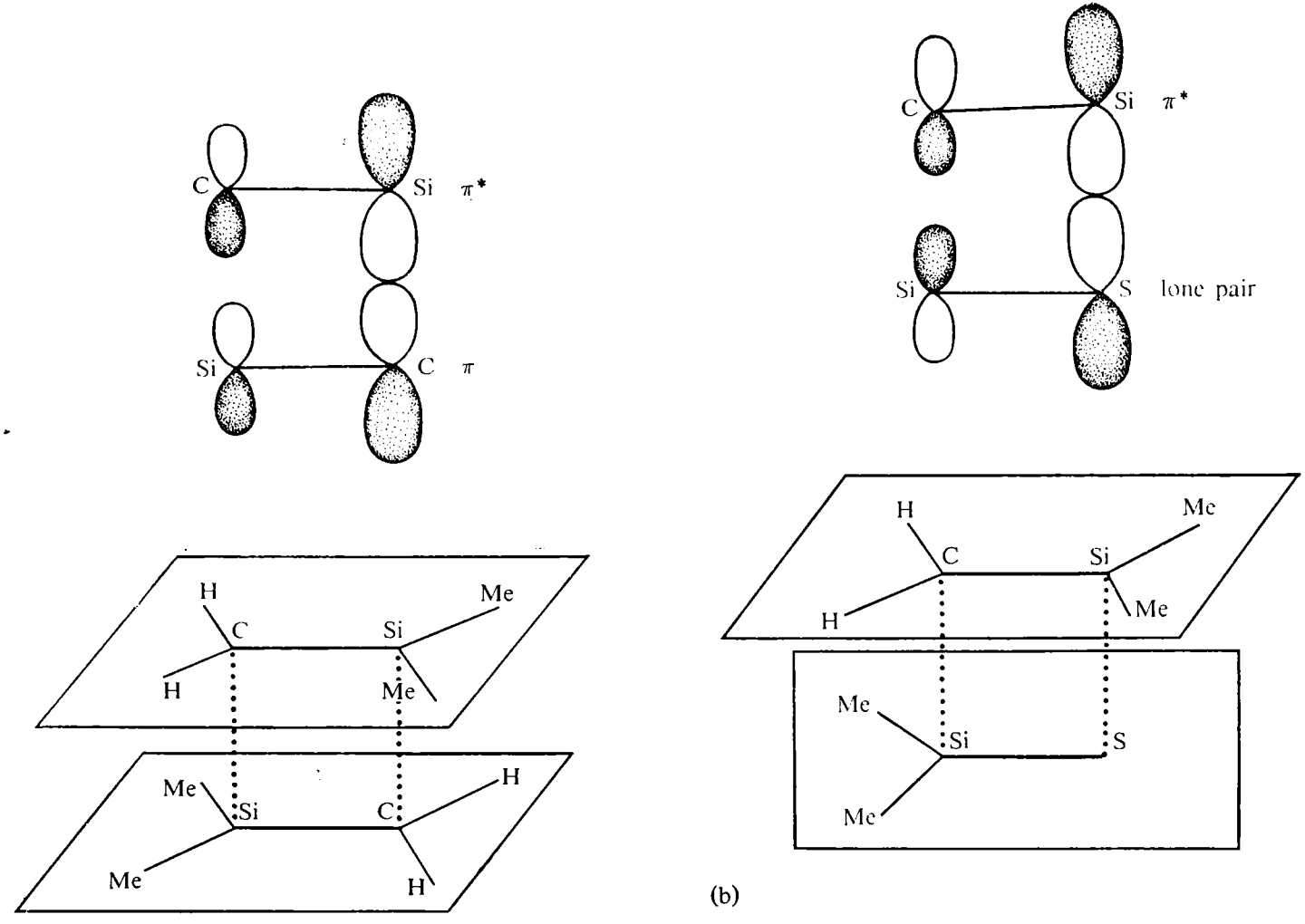
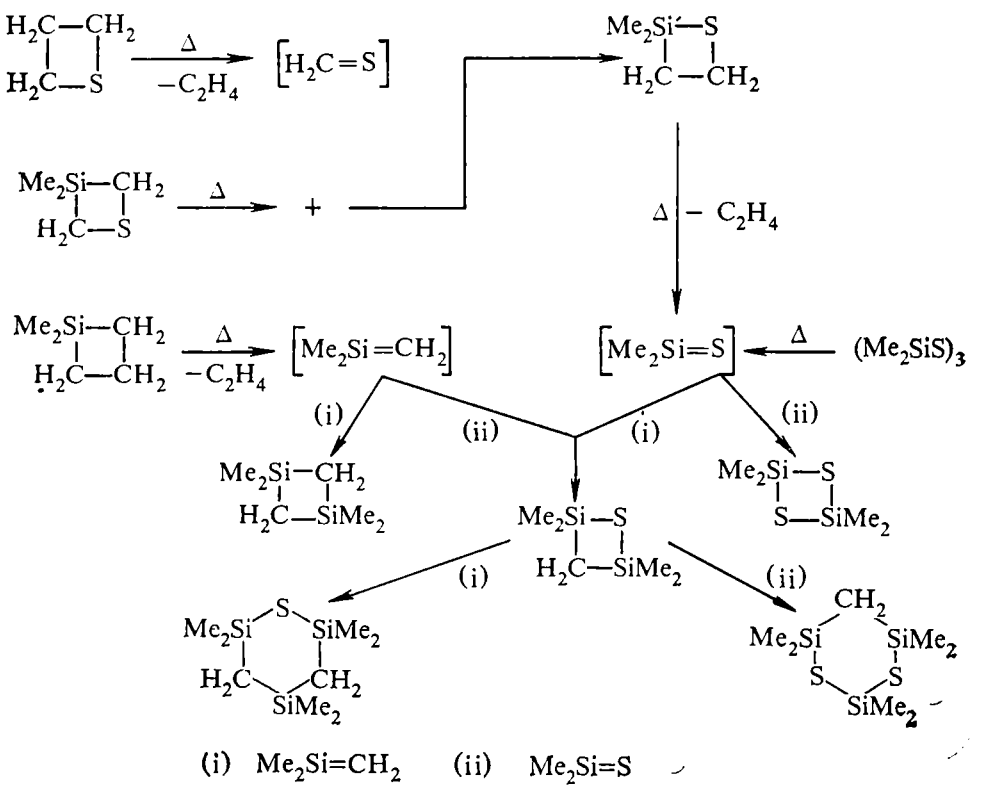


Figure 2. MO representation of (a) cyclodimerization of $Me_2Si{=}CH_2$ and (b) [2 + 2]-cycloaddition of $Me_2Si{=}CH_2$ to $Me_2Si{=}S$.

rolysis of DMSCB with cyclosilthianes has revealed [88-90] that DMSE and dimethyl silanthione (DMST) readily enter into the [2 + 2]-cycloaddition reaction yielding 2,2,4,4-tetramethyl-2,4-disilathietane and get inserted into the Si—S bond of the cycloadduct (Scheme 5). Similar products are also obtained upon copyrolysis of DMSCB with thietane (5:1). A dimer DMST will be produced if reactions involve stoichiometric amounts of DMSE and thioformaldehyde (as with the pyrolysis of 3,3-dimethyl-3-silathietane). The mechanisms for [2 + 2]-cyclodimerization of silaalkenes and [2 + 2]-cycloaddition of silaalkenes to silanthiones appear to be different.

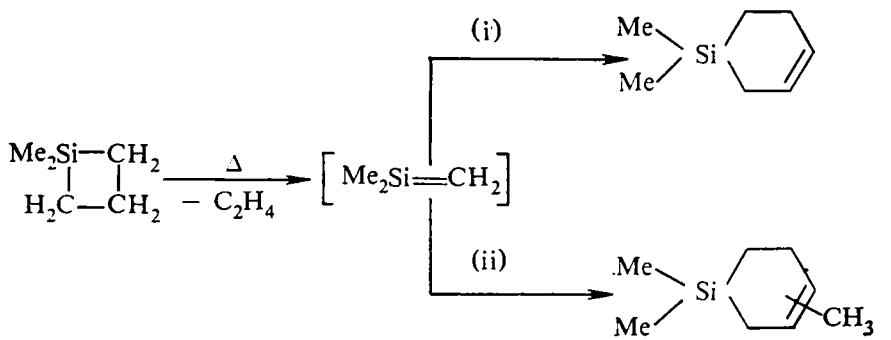
Scheme 5



The former reaction proceeds thermally as a non-concerted process, the latter is a thermally allowed concerted process (Fig. 2). Theoretical analysis of the reactivity of DMSE in [2 + 2]-cycloaddition to ethylene, DMSE, thioformaldehyde, and DMST by the perturbation Molecular Orbital method has shown [89, 90] that the PMO energy (E_{PMO}, kcal/mol) is the lowest in reaction with ethylene (0.92), the reactions with DMSE and DMST proceed faster (6.19 and 13.4, respectively), and the reactions of DMSE with thioformaldehyde and DMST cyclodimerization proceed most rapidly (20.6 and 23.3, respectively).

Of special interest are reactions of silaalkenes with conjugated dienes (the Diels-Alder type reactions) [33, 34, 106]. During pyrolysis of DMSCB carried out in the presence of a threefold excess of butadiene or isoprene, cyclodimerization of DMSE was completely suppressed, and the reaction proceeded as [2 + 4]-cycloaddition (Scheme 6.)

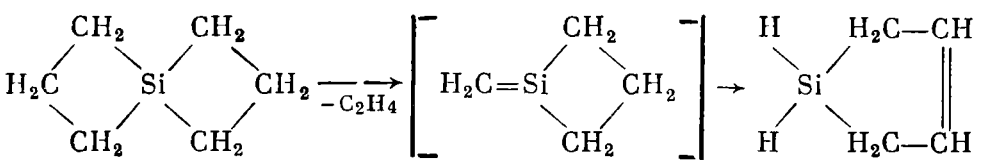
Scheme 6



(i) $CH_2=CHCH=CH_2$ (ii) $CH_2=C(CH_3)-CH=CH_2$

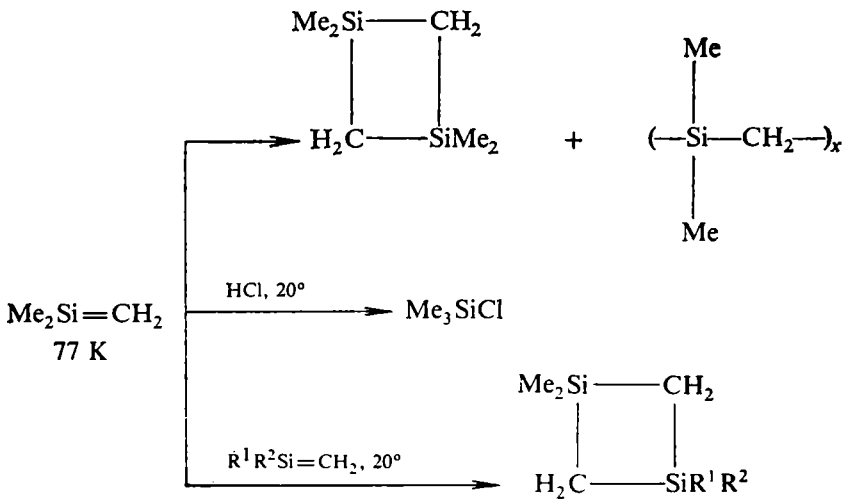
In certain cases silaalkenes rearrange [37], as follows:

Scheme 7



The bimolecular reactions of DMSE can be slowed down by the pyrolysis of DMSCB at low pressure, and by condensating the products on a surface cooled to 65-77 K. In so doing, it becomes possible to stabilize the DMSE monomer even at comparatively not very low temperatures. Contribution of the cyclodimerization reaction decreases on lowering pressures from 10^{-1} torr to 10^{-3} torr. This is indicated by an increase in the concentration ratio of the primary decomposition product (C_2H_4) to TMDSCB, a product of DMSE cyclodimerization [39]. Condensing a chemical trap on the frozen pyrolysis products and defrosting the "sandwich" so formed yields the expected adducts with DMSE (Scheme 8). In the absence of traps a DMSE polymer was obtained in addition to TMDSCB [67, 91].

Scheme 8



(1) $R^1 = R^2 = CD_3$

(2) $R^1 = Me$, $R^2 = CH_2CH_2CF_3$

Table 1 lists the rate parameters of some addition reactions to DMSE in a gas phase.

Table 1. The Arrhenius Parameters for Some Addition Reactions Involving $Me_2Si=CH_2$

Reagent	log *A*	*E*, kcal/mol	*K* (800K) [a]	References
$Me_2Si=CH_2$	6.6	0 (2.7b)	3.55×10^6	[55]
$H_2C=CH_2$	6.2	14.5	1.77×10^3	[55]
$CH_3CH=CH_2$	5.2	8.4	8.2×10^2	[107]
Me_3SiOMe	5.3	1.5	7.7×10^4	[100]
H_2O	—	11.5	—	[108]
HCl	7.5	2.4	7.0×10^6	[96]
HBr	7.4	8.6	1.1×10^5	[96]
O_2	7.6	3.6	4.2×10^6	[96]

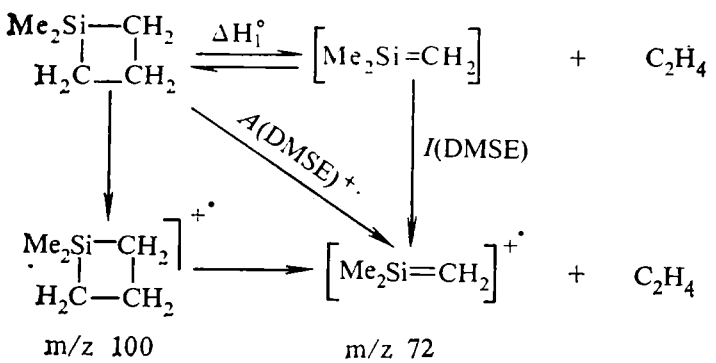
(a) litre·mol^{-1}·s^{-1}, (b) Ref. [108]

Thus, while kinetic studies consistent with silaalkene participance have not provided any alternative explanation to the mechanism of thermal decomposition of monosilacyclobutanes, chemical studies have demonstrated a resemblance between the chemical properties of silaalkenes and olefins in the reactions of addition to the silicon-carbon double p_π-p_π bond.

4. THERMOCHEMICAL STUDIES ON THERMAL DECOMPOSITION AND DISSOCIATIVE IONIZATION OF MONOSILACYCLOBUTANES. HEAT OF FORMATION AND IONIZATION POTENTIAL OF 1,1-DIMETHYL-1-SILAETHYLENE. Si=C π-BOND ENERGY

The energy characteristics of DMSE (heat of formation and ionization potential) were first derived [58, 91] from thermochemical studies on thermal decomposition and dissociative ionization of DMSCB. This is presented in Scheme 9 by the Born-Haber

Scheme 9



thermochemical cycle. The heat of formation and ionization potential of DMSE (underlined) are associated with the enthalpy of reaction (1) by Eqs. (11) and (12)

$$\Delta H_1^\circ = \Delta H_f^\circ \underline{(\text{DMSE})} + \Delta H_f^\circ (C_2H_4) - \Delta H_f^\circ (\text{DMSCB}) \quad (11)$$

$$\Delta H_1^\circ = A\,(\text{DMSE})^{+\cdot} - \underline{I(\text{DMSE})} \quad (12)$$

The following: kinetic data [8, 9, 55], heat of formation of DMSCB, found calorimetrically by combustion of samples in the presence of benzotrifluoride (ΔH_f° (DMSCB)$_{liq}$ = −27.5 ± 1.3 kcal/mol; ΔH_f° (DMSCB)$_g$ = −19.8 ± 1.4 kcal/mol) [44, 51, 52]; heat of evaporation of DMSCB (7.7 kcal/mol) [40]; and the appearance potential of the ion *m/z* 72 $(\text{DMSE})^{+\cdot}$ in the mass spectrum of DMSCB (9.61 ± 0.05 eV) determined by photoionization [43, 53] were used in the calculations. According to the kinetic data, ΔH_1° = 47.8 ± ± 4.8 kcal/mol [58, 91]. Substituting the known values into Eq. (11) gives ΔH_f° (DMSE)$_k$ based on the kinetic data:

$$(47.8 \pm 4.8) = \Delta H_f^\circ (\text{DMSE})_k + 12.5\ [\text{Ref. } 109] - (-19.8 \pm 1.4)$$

$$\Delta H_f^\circ (\text{DMSE})_k = 15.5 \pm 6.2\ \text{kcal/mol}$$

Now using Eq. (12), we can estimate the value of the ionization potential of DMSE:

$I(\text{DMSE}) = (9.61 \pm 0.05) - (47.8 \pm 4.8)/23.06$

$I(\text{DMSE}) = 7.5 \pm 0.3$ eV

Calculated in 1975 [58], this value of I(DMSE) is in fairly good agreement with I(DMSE) = 7.71 ± 0.03 eV measured in studying reaction (1) by photoelectron spectroscopy [92]. Now substituting the revised value of I(DMSE) into Eq. (12), we can independently derive ΔH_1°:

$\Delta H_1^\circ = [(9.61 \pm 0.05) - (7.71 \pm 0.03)] \cdot 23.06$

$\Delta H_1^\circ = 43.8 \pm 1.8$ kcal/mol

As is seen, satisfactory compliance with ΔH_1° obtained from kinetic data is also observed. Substituting $\Delta H_1^\circ = 43.8 \pm 1.8$ kcal/mol into Eq. (11) gives ΔH_f° (DMSE)$_g$ based on spectroscopic (PI/PES) data

$\Delta H_f^\circ (\text{DMSE})_g = 11.5 \pm 3.2$ kcal/mol

Since photoionization mass spectrometry and photoelectron spectroscopy are fairly accurate techniques for determining A (DMSE) and I(DMSE), respectively, the value of $\Delta H_1^\circ = 43.8 \pm 1.8$ kcal/mol may be considered highly reliable. Therefore the accuracy with which ΔH_f° (DMSE)$_g$ is calculated by Eq. (11) wholly depends on the reliability of the value of ΔH_f° (DMSCB). The latter, in our case, was ensured by combustion of DMSCB in benzotrifluoride; the application of this calorimetric method makes it possible to avoid errors caused by incomplete combustion of organosilicon compounds to SiO_2. Reliance on ΔH_f° (DMSCB) = −33 kcal/mol in the calculation made by Eq. (11) [109, 110] gives ΔH_f° (DMSE) = −1.7 kcal/mol, which, as ΔH_f° (DMSE) = 0.48 kcal/mol [111], appears to be underestimated. The recently determined value of the heat of formation of DMSE (7 ± 5 kcal/mol) [112, 113] is fairly close to ours.

Walsh used Eqs. (1) and (3) to estimate the lower and upper limits of the carbon-silicon π-bond energy in DMSE: $26 < D_\pi$ (Si=C) < 46 [114]. Later, the π-bond energy was estimated to be equal to 37 kcal/mol [113]. Similar calculations of D_π (Si=C) by the enthalpies of reactions (1), Eq. (13), and (2), Eq. (14), are given below:

$\Delta H_1^\circ = D\,(\text{Si}-\text{C}) + D\,(\text{C}-\text{C}) - D_\pi\,(\text{Si}=\text{C}) - D_\pi\,(\text{C}=\text{C}) -$

$- E_s\,(\text{DMSCB})$ (13)

$(43.8 \pm 1.8) = 88.2$ [Ref. 112] $+ 82$ [Ref. 112] $-$

$- D_\pi$ (Si=C) $- 59$ [Ref. 115] $- 25.9$ [Ref. 52]

D_π (Si=C) = 41.5 kcal/mol

$$\Delta H_2^\bullet = \Delta H_f^\bullet (\text{TMDSCB}) - 2\Delta H_f (\text{DMSE}) = 2D_\pi (\text{Si=C}) - 2D (\text{Si—C}) + E_s (\text{TMDSCB}) \quad (14)$$

$$(-53.9 \pm 2.4 \text{ [Ref. 51]}) - 2 (11.5 \pm 3.2) = 2D_\pi (\text{Si=C}) - 2 \times 88.2 \text{ [Ref. 112]} + 17.7 \text{ [Ref. 52]}$$

$$D_\pi (\text{Si=C}) = 40.9 \text{ kcal/mol}$$

These values of D_π (Si=C) indicate that the silicon and methylene carbon atoms of the DMSE are actually double-bonded ($Me_2Si{=}CH_2$), i.e. the alternative biradical structure ($Me_2\dot{S}i—\dot{C}H_2$) is ruled out. The energy of the Si=C π-bond makes up approximately two-thirds of that of the C=C π-bond.

Thus, thermochemical studies of the processes of thermal decomposition and dissociative ionization of 1,1-dimethyl-1-silacyclobutane yielded reliable energy characteristics of 1,1-dimethyl-1-silaethylene, which is the first representative of a new structural class of silaalkenes in organosilicon chemistry.

5. SPECTROSCOPIC STUDIES OF SILAALKENES GENERATED IN THERMAL DECOMPOSITION OF MONOSILACYCLOBUTANES

The results cited of the research into the thermal decomposition of monosilacyclobutanes using kinetic, chemical, and thermochemical approaches have made it possible to identify and characterize silaalkenes—unstable intermediate compounds which display a pronounced tendency towards bimolecular addition reactions involving the silicon-carbon double bond.

Further studies into the chemistry of silaalkenes were aimed at elucidation of the nature of the silicon-carbon double p_π-p_π bond by spectroscopic methods. This problem has been solved by using reaction (1), which, being highly selective, offered a unique opportunity for generation of 1,1-dimethyl-1-silaethylene, $Me_2Si{=}CH_2$. To suppress the secondary reaction (2) and introduce monomeric DMSE into the spectrometer, very low pressure pyrolysis (VLPP) [116] or its combination with matrix isolation (VLPP/MI) was used, depending on the type of spectroscopic analysis. During VLPP of 1,1-dimethyl-1-silacyclobutane $Me_2Si{=}CH_2$ was studied in the gas phase by mass spectrometry [54, 55, 117], photoelectron spectroscopy [92, 118], and electron diffraction [119].

By the VLPP/MS technique we established a relationship between the relative intensity of the peak of the DMSE ion (*m/z* 72) and the conversion of DMSCB: the higher the conversion of DMSCB, the higher the I_{72}/I_{100} ratio. This was proved to be associated with direct observation of DMSE thermally generated from DMSCB [54, 55].

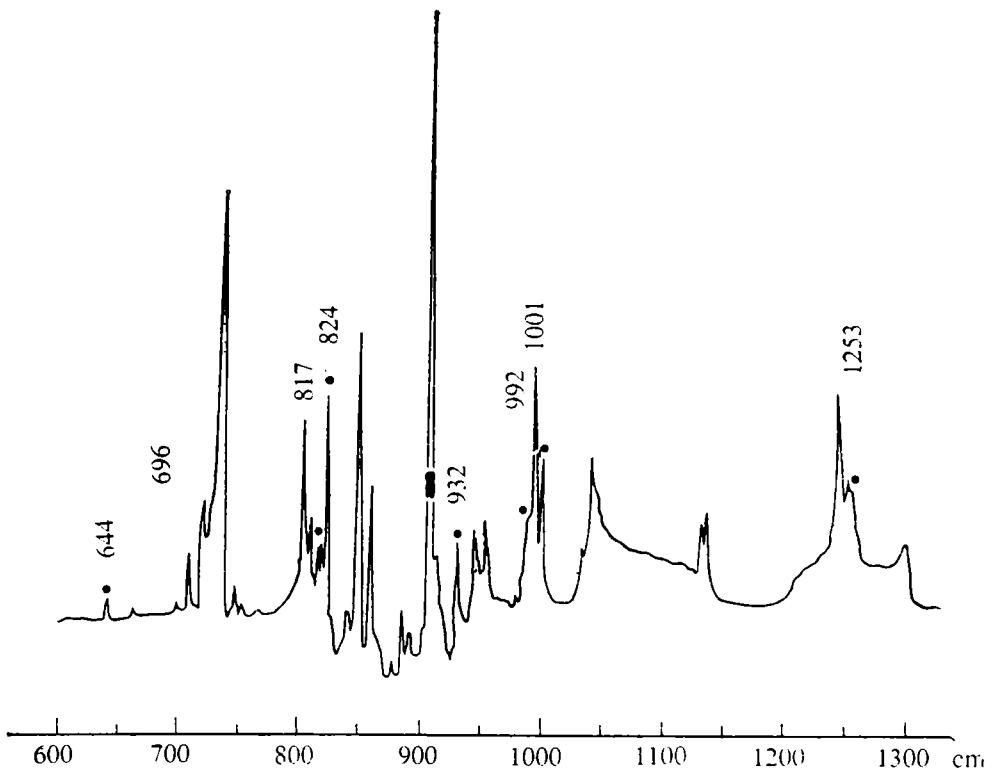
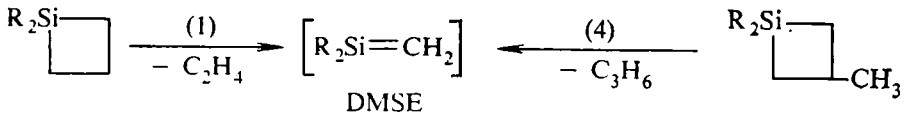


Figure 3. IR spectrum of Ar-matrix isolated pyrolysis products of 1,1,3-trimethyl-1-silacyclobutane (absorption bands of $Me_2Si{=}CH_2$ are designated by asterisks).

Also, in an analogous experiment one succeeded in estimating the ionization potential of DMSE (7.7 ± 0.4 eV) [117]. Later, during pyrolysis of DMSCB the ionization potential of DMSE (eV) was determined by the VLPP/PES method: VIP 8.3 ± 0.05 [118], 7.98 ± 0.01 [92]; AIP 8.00 ± 0.05 [118], 7.71 ± 0.03 [92]. As is seen, the last value of AIP is in good agreement with the earlier estimated value (7.5 ± 0.3 eV [58, 91]). The VLPP/MI/IR method was used [120, 121] to take the spectrum of the pyrolysis products of DMSCB. The 1259, 1251, 1003.5, 825.2, 817.5, and 642.9 cm^{-1} bands were assigned to DMSE because with an increase in temperature of the Ar matrix from 10 to 40 K they disappeared with the appearance of TMDSCB bands (that is, reaction (2) occurred). Of these, 642.9 cm^{-1} was assigned to the stretching vibration of $Si{-}CH_3$, 825.2 cm^{-1}, to the deformation vibration of ∠ HCSi, and 1003.5 cm^{-1}, to the deformation vibration of ρ-CH_2 (wagging). The band of the Si=C double bond stretching vibration was not identified [121]. The aim of our work [19, 60, 65, 66, 67, 75], whose main results were reported in 1979-1980, was to search for the band of the Si=C double bond stretching vibration in the IR spectrum of 1,1-dimethyl-1-silaethylene characterizing affiliation of DMSE to the structural

class of silaalkenes. Two sources of DMSE (DMSCB and 1,1,3-TMSCB) and two sources of DMSE-d_6 (DMSCB-d_6 and 1,1,3-TMSCB-d_6) were studied by the VLPP/MI/IR method:



(15)

R = CH_3 (DMSE): 1253, 1001, 992, 932, 824, 817, 696, 644 cm^{-1}

R = CD_3 (DMSE-d_6): 1012, 985, 929, 768, 722, 718, 683, 543 cm^{-1}

The IR spectrum of the 1,1,3-TMSCB VLPP products isolated in the Ar-matrix is shown in Fig. 3 where the absorption bands of DMSE are marked with asterisks [19, 66]. A similar investigation was carried out elsewhere [122]. Notwithstanding some variations, a reasonably good agreement is observed, on the whole, between the results of these two experiments. We assumed the DMSE molecule to have a C_{2v} symmetry, that is, to be isostructural to isobutylene (the correctness of this choice was later confirmed by the ab initio calculations [123]), and computed the frequencies and modes of normal vibrations. As a result, the first theoretical interpretation of the vibrational spectra of DMSE and DMSE-d_6 was achieved [65, 66]. Assignment of the DMSE absorption bands is given in Table 2.

Table 2. Assignments of Bands in the IR Spectrum of $Me_2Si=CH_2$

Symmetry	Frequency, cm^{-1}	Assignment
A_1	1253	Deformation vibration ∠HCH and ∠HCSi
A_1	1001	Stretching vibration Si=C
B_2	992	Deformation vibration ∠HCSi
B_2	932	Non-planar deformation vibration $Si=CH_2$ group
B_1	824	Deformation vibration ∠HCSi
A_1	817	Deformation vibration ∠HCSi
B_1	696	Stretching vibration Si—C(H_3)
A_1	644	Stretching vibration Si—C(H_3)

In particular, a study was made into the dependence of the Si—C bond stretching vibration frequency on variations in the force constant f_{SiC} between 3.2 and 8.3 mdyn/A, which corresponds to a change in the order of the SiC bond from 1 to >2 (Fig. 4). As is seen, ν_{SiC} cannot exceed 1200 cm^{-1} for any realistic values of f_{SiC}. Assuming

that in going from a single to a double bond f_{SiC} changes in a similar manner as f_{CC}, we obtained a value of f_{SiC} close to 5.8 mdyn/A, which suggests that the value of ν_{SiC} equals 1014 cm^{-1}. This is very close to the band (1001 cm^{-1}). Therefore we have assigned the 1001 cm^{-1} band in the spectrum of $Me_2Si{=}CH_2$ to the stretching vibration of the silicon-carbon double bond [19, 60, 65, 66] (almost at the same time similar conclusions were drawn by the authors of Refs. [122, 125] with different initial assumptions).

The curve of Fig. 4 can be used to predict ν_{SiC} for the molecules of silaalkenes only when ν_{SiC} is characteristic. An analysis of the

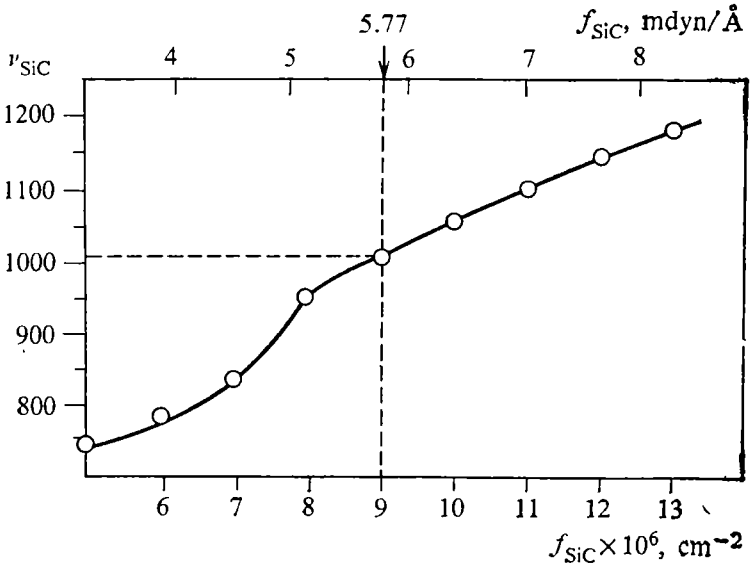


Figure 4. Theoretical relationship between the frequency of the stretching vibration ν_{SiC}, and variations in the force constant, f_{SiC}, in the IR spectrum of 1,1-dimethyl-1-silaethylene.

distribution of potential energy in normal coordinates computed in [65] suggests that for the DMSE and silaethylene ($H_2Si{=}CH_2$) molecules the stretching vibration is quite characteristic, that is the participation of the SiC bond stretch coordinate amounts to 89 and 96 per cent, respectively. By contrast, for the DMSE-d_6, DMSE-d_2 ($(CH_3)_2Si{=}CD_2$), and DMSE-d_8 ($(CD_3)_2Si{=}CD_2$) molecules, the ν_{SiC} vibration proved to be noncharacteristic due to mixing with the deformation coordinates $\angle$HCH and $\angle$HCSi in DMSE-d_6, with $\angle$Si=CD in DMSE-d_2, and as with $\angle$HCH, $\angle$HCSi, and $\angle$Si=CD in DMSE-d_8. This is the reason why an apparent increase in the frequency of vibrations ν_{SiC} up to 1012 cm^{-1} for DMSE-d_6 [19, 60, 65, 66, 122, 125] and 1117.5 and 1112 cm^{-1} for DMSE-d_2 and DMSE-d_8 is observed in the experimental spectra of the silaalkenes [125]. In fact, the IR spectra of these molecules exhibit two resonating levels each belonging to the mixed vibrations ν_{SiC} with these angles, the

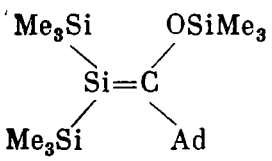
second frequencies being much lower: 985 [19, 60, 65, 66], 895.5 and 866.5 cm^{-1} [125].

Thus, the spectroscopic studies wholly corroborate the conclusions drawn in this paper about silaalkenes as about silicon analogues of olefins, and show that the band of the silicon-carbon double bond stretching vibration in the IR spectrum of DMSE appears at about 1001 cm^{-1}.

6. CONCLUSION

The problem of the existence of compounds having a double p_π-p_π bonded silicon atom, as formulated in the 1960s, has virtually been resolved today. Now numerous highly reactive intermediates containing a double p_π-p_π bonded silicon atom have been found in various gas- and liquid-phase reactions. With respect to unimolecular decomposition most of them are thermodynamically stable molecules. Effective p_π-p_π bonding between silicon and carbon atoms is responsible for the similarity of chemical properties of silaalkenes and olefins. What distinguishes silaalkenes from their carbon analogues is their higher reactivity and lower π-bond energy.

Currently, research is occupied with the search for new methods of generating silaalkenes, and the study of their physical and chemical properties, as well as their reactivity. Silaalkenes have been useful in the development of novel preparative synthetic procedures, and in freshly interpreting some known reactions in organosilicon chemistry. Synthesis of solid silaalkenes (silenes [126] and disilenes [127]) stabilized by bulky substituents has been a breakthrough, indeed:



$Mez_2Si{=}SiMez_2$

Ad=adamantyl Mez=mesityl

These silaalkenes do not dimerize but occur as crystalline monomers. Nevertheless, they exhibit exceedingly high reactivity in relation to oxygen and air moisture, and readily enter into other reactions characteristic for silaalkenes. Of the great body of silaalkenes occurring mostly as transient reactive intermediates, these compounds are a remarkable exception.

In summary, the first evidence for the existence of silaalkenes and their identification via thermal decomposition of monosilacyclobutanes have revealed the previously unknown property of silicon atom to form p_π-p_π double bonds with carbon. This in turn has resulted in the wide-spread development of new areas in organosilicon chemistry.

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5 Ionic Polymerization of Organylcyclosiloxanes

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1. INTRODUCTION

Studies in the field of ionic polymerization and copolymerization of organylcyclosiloxanes (OCS) are being intensely pursued since this process underlies the production of commercial organosilicon, and siliconorganoelement oligomers and polymers [1].

Ionic polymerization of OCS is a complex catalytic process. Therefore synthetic achievements in this domain are based on the results of detailed studies of the reaction and on finding optimum conditions of carrying it out.

The different factors that influence the polymerization and copolymerization of OCS in the presence of electrophilic and nucleophilic initiators are analyzed in this article.

2. POLYMERIZATION AND COPOLYMERIZATION OF ORGANYLCYCLOSILOXANES IN THE PRESENCE OF ELECTROPHILIC INITIATORS

Sulphuric acid was first used for polymerization of oligocyclodimethylsiloxanes [2]. Later on, Lewis acids and other electrophilic reagents were employed as initiators [3].

Octamethylcyclotetrasiloxane (D_4) interacts with aluminium chloride to give polydimethylsiloxanes and α,ω-dichlorooligodimethylsiloxanes [4, 5]. The reaction of $AlBr_3$ with D_4 at 150 °C, depending on its conditions and the ratio of the reactants, results in dimethyldibromosilane, a rarely available α,ω-dibromooligodimethylsiloxanes, and a crystalline compound of the following composition $[OMe_2SiOSiMe_2OAlBr]_2AlBr_3$ [6]; the structure of the compound was defined more accurately in later studies [7].

At temperatures up to 100 °C, anhydrous $FeCl_3$ does not cause polymerization of D_4 or its telomerization with dimethyldichlorosilane. Water and hydrogen chloride are active cocatalysts for $FeCl_3$. For this reason, $FeCl_3$, when in the presence of these reactants, actively initiates polymerization processes. The active role that traces of water play in the reaction of Fe_2O_3 with dimethyldichlorosilane which gives α,ω-dichlorooligodimethylsiloxanes and $FeCl_3$ was also

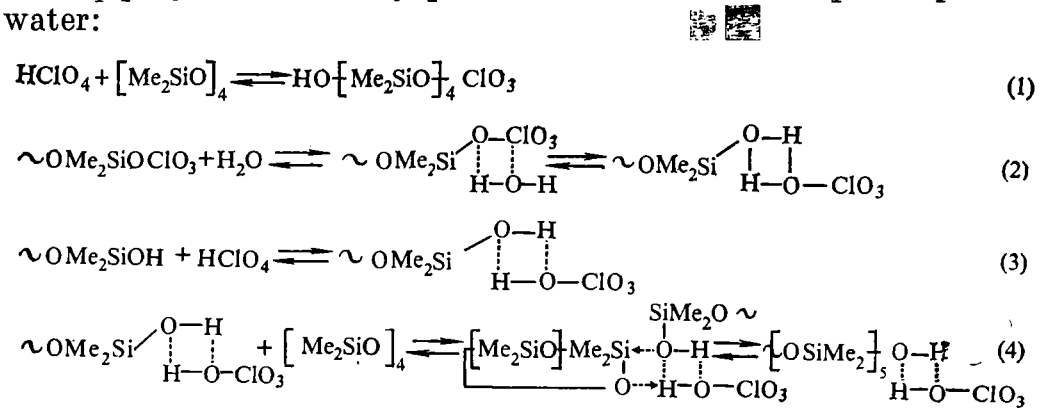
disclosed. In the absence of traces of H_2O or HCl, the reaction practically does not go [8]. The reaction between D_4 and $FeCl_3$ in the presence of bromine proceeds in a very peculiar manner. The reaction involves both breakdown of the Si—C bond with the formation of methyl bromide, and breakdown of the Si—O bond and the polymerization of D_4 which results in the formation of a partly cross-linked polymeric product [9].

The influence of proton and aprotic polar additives on the polymerization of D_4 with an electrophilic initiator like perchloric acid was studied [10]. The polymerization was run at 96 °C in the presence of 33, 55.7, and 73% aqueous solutions of $HClO_4$. In all cases there was an induction period observed at the beginning of the reaction, its duration increasing at lower concentrations of $HClO_4$. This is obviously due to a decrease in the rate of formation of the polymerization reaction sites which was caused by diminished activity of the acid at lower concentrations.

The addition of an equimolar amount of CH_3COOH to $HClO_4$ increases the reaction rate and shortens the induction period. The introduction of the same amounts of dimethyl diethylene glycol and particularly of dimethylformamide (DMFA) retards the polymerization of D_4.

The decrease in the reaction rate in the presence of aprotic polar additives is explained by their ability to bind the proton by a hydrogen bond.

These experimental data suggest the following simplified scheme for D_4 polymerization by perchloric acid with the participation of water:



(1)

(2)

(3)

(4)

Reaction (1) is the slowest and is responsible for the existence of the induction period. A strong shift of reaction (1) to the left causes the number of growing chains to be smaller than the concentration of the initiator; therefore, a certain amount of the initiator remains in the free form.

The copolymerization of D_4 with 2,4,6,8-tetraphenyl-4,6,8-trimethylcyclotetrasiloxane in the presence of various amounts of sulphuric acid was studied [11]. The choice of the initiator for this

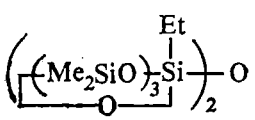
reaction is greatly restricted because all nucleophilic initiators are unsuitable due to the high reactivity of the ≡Si—H group with respect to the siloxane bond, when in the presence of nucleophiles [12, 13]. Among electrophilic initiators, $SnCl_4$, $Al_2(SO_4)_3 \cdot 2H_2O$ activated by sulphuric acid, and 96% H_2SO_4 were tested. The activity of these agents decreases in this series: $H_2SO_4 > Al_2(SO_4)_3 \cdot 2H_2O > SnCl_4$. In the course of the reaction, $SnCl_4$ is reduced to $SnCl_2$. Aluminium sulphate initiates the process at abt. 100 °C and sulphuric acid at 20-70 °C. In the presence of sulphuric acid copolymers with a molecular weight ranging between 1.2×10^5 and 4.2×10^5 were obtained in a 70-78% yield [14]. According to ^1H NMR and IR spectroscopy data and also to the results of precipitation chromatography experiments, they are statistical copolymers.

3. POLYMERIZATION AND COOPOLYMERIZATION OF ORGANYLCYCLOSILOXANES IN THE PRESENCE OF NUCLEOPHILIC INITIATORS

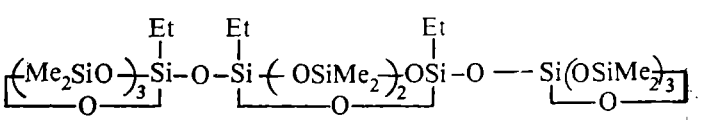
Studies of the polymerization of OCS in the presence of nucleophilic initiators started in 1947 [15]. The process was consequently studied in more detail [3].

We studied the reactivity of OCS in the presence of 0.5% KOH at 130 °C. OCS contains dimethylsiloxane and other diorganylsiloxane units: 2,4-divinyl-2,4,6,6,8,8-hexamethyl-, 2,4,6-trivinyl-2,4,6,8,8-pentamethyl-, 2,4,6,8-tetravinyl-2,4,6,8-tetramethyl-, 2,2-diethyl-4,4,6,6,8,8-hexamethyl-, and 2-phenyl-2-ethyl-4,4,6,6,8,8-hexamethylcyclotetrasiloxane [16]. An increase in the volume of the substituents at the silicon diminishes the anionic polymerization ability of the OCS. The larger the number of electron acceptor vinyl groups in methylvinylcyclosiloxanes, the higher the reactivity of the OCS.

The influence of alkylsilsesquioxane fragments in OCS on the rate of anionic polymerization was studied in a sample of bi- and tricyclic compounds (I and II) in the presence of 0.3% KOH [17].



I



II

I and II polymerize at room temperature, i.e. much easier than cyclodimethylsiloxanes. The rate of the reaction increases as the number of ethylsilsesquioxane units in the molecule increases. This is due to silicon's strong tendency in the alkylsilsesquioxane fragment to form a transition complex with the nuclephilic centre of the growing chain because of the higher electrophility of this atom. The presence

of alkylsilsesquioxane units also raises the thermal stability of the polymers [18].

Polymerization of OCS that contained not only dimethylsiloxy- and methylphenylsiloxy units but also methyl(dihydrodicyclopentadienyl)siloxy units was studied at 80-90 °C in the presence of 0.1% KOH in blocks. The copolymerization of these compounds with a mixture of *cis* and *trans* isomers of 2,4,6-trimethyl-2,4,6-triphenylcyclotrisiloxane (A_3) was also investigated [19]. Transparent high-molecular polymers and copolymers (m.w. 4.2×10^5-5.5×10^5) highly soluble in various organic solvents were obtained in these experiments. The polymers get easily cross-linked when stored whereas the copolymers remain stable.

A polymer prepared from pentamethyl(tetrahydrocyclopentadienyl)cyclotrisiloxane, in contrast to its unsaturated analogue, does not undergo cross-linking. This indicates that introduction of methyl(dihydrodicyclopentadienyl)siloxy units into the polymer chain gives polydiorganylsiloxanes the ability of being cross-linked under mild conditions. The modification of rubber blends that are based on dimethylmethylvinylsiloxane rubber with polymers containing methyl(dihydrodicyclopentadienyl)siloxy units increases their ability to vulcanize [20].

The effect that the reaction conditions have on polymerization in solution, in blocks, and in crystals was studied on an example of *cis*-A_3 and a mixture of A_3 isomers [21-23].

The initial step of α-hydroxy-ω-(tetramethylammoniumoxy)polymethylphenylsiloxane-initiated polymerization of *cis*-A_3 in benzene yields polymer going up to 98%. However, as the process continues, the yield of the polymer and its viscosity drop. The high yield at the beginning is a result of faster A_3 polymerization, as compared with the depolymerization reaction rate, and of the low equilibrium A_3 concentration. The low-molecular polymerization products are unstrained eight-membered and higher methylphenylcyclosiloxanes. After the removal of benzene from the reaction mixture, the viscosity of the polymer and its yield grow. This is due to the shift of the OCS-polymer equilibrium towards the formation of the latter.

The dependence of the polymer yield on its viscosity in the course of block polymerization of *cis*-A_3 at temperatures above the melting point (100-110 °C) also features an extremum.

The polymerization of *cis*-A_3 and a mixture of A_3 isomers in the presence of potassium trimethylsilanolate (PTMS), potassium or tetramethylammonium polymethylphenylsiloxane-α,ω-diolate (TMAPS), and also of hexamethylcyclotrisiloxane (D_3) in the presence of Me_3SiOK in crystal phase at 20-70 °C gives polymers with η_{sp} ranging between 0.29 and 1.66. However, the process is very slow, particularly at 20 °C.

Because tetraorganylammonium or tetraorganylphosphonium organylsiloxane-α,ω-diolates are promising polymerization initiators (this is a result of their high activity and capability of subsequent thermal decomposition [24]) their catalytic activity, thermal decomposition, and the effect of the decomposition products on the polymers formed were studied [25-27].

The thermal decomposition of tetraorganylammonium polydimethylsiloxane-α,ω-diolates (TOAS) with different substituents at the nitrogen is a first-order reaction with respect to the current concentrations of the end groups

$$(W_{NR_4} = -k_{NR_4}[NR_4] \quad (5)$$

The stability of the TOAS end groups decreases in the following way:

	Me_4N	$Me_3(PhCH_2)N$	>	Et_4N	>	Bu_4N	>
$10^5 \times k^{80°C}_{NR_4}$, s^{-1}	1.1	1.1		44		50	

	Me_3PhN	>	$BuMe_2PhN$	>	$EtMe_2PhN$		
$10^5 \times k^{80°C}_{NR_4}$, s^{-1}	110		190		250		

The length of the polydimethylsiloxane chain in TOAS does not have a strong influence on the rate of their thermal decomposition.

Siloxanediolates containing a hydrogen in the β position in the substituent at the nitrogen decompose with the formation of polydimethylsiloxane-α,ω-diols, water, unsaturated hydrocarbons, and an amine:

$$R_2R'R^2NO\left[Me_2SiO\right]_nNR_2R'R^2 \xrightarrow{t} C_mH_{2m} + \left[Me_2SiO\right]_z + R_2R'N + HO\left[Me_2SiO\right]_pH \quad (6)$$

$R_2R^1R^2 = Et_4$, Me_2EtPh; $m = 2$; $n = 10\text{-}200$; $p = 10\text{-}200$; $z = n - p = 4{,}5$

$R_2R^1R^2 = Bu_4$, $BuMe_2Ph$; $m = 4$; $n = 10\text{-}200$; $p = 10\text{-}200$; $z = n - p = 4{,}5$

Siloxanediolates having no substituents with a hydrogen in the β position in the tetraorganylammonium group decompose to give amines and α,ω-dialkoxypolydimethylsiloxanes:

$$Me_2R'R^2NO\left[Me_2SiO\right]_nNR'R^2Me_2 \xrightarrow{t} R^2O\left[Me_2SiO\right]_pR^2 + Me_2R'N + \left[Me_2SiO\right]_z \quad (7)$$

$R^2 = Me$, $PhCH_2$; $R^1 = Me$; $z = 4{,}5$; $n = 10\text{-}200$

$R^2 = Me$; $R^1 = Ph$; $n = 10\text{-}200$

TOAS-initiated polymerization of D_3 is not at equilibrium at 50 °C. This is indicated by the absence of higher cycles in the reaction products and by a high yield of the polymer (96-99%). The reaction rate is described by

$$W_{D_3} = -k_{D_3}[D_3] \quad (8)$$

The end groups in TOAS affect the k_{D_3} values. The decrease is in this order ($[NR_4]_0 = 6 \times 10^{-4}$ g-eq/litre) [27]:

$$10^3 \times k_{D_3}^{50°C},\ s^{-1}: \quad \underset{5.5}{Bu_4N} > \underset{4.9}{BuMe_2PhN} > \underset{4.2}{Et_4N} > \underset{3.8}{Me_4N} > \underset{3.7}{EtMe_3PhN} > \underset{3.3}{Me_3(PhCH_2)N} > \underset{1.7}{Me_3PhN}$$

Thermogravimetric analysis of polymethylphenylsiloxanes with tetraorganylammonium or -phosphonium end groups shows that the highest thermal stability is featured by polymers forming products of lowest basicity in the course of decomposition [26].

Hydroxyl-containing compounds introduced into the reaction medium or present as impurities may take an active part in TOAS-initiated polymerization.

For instance, during the polymerization of *cis*-A_3 in benzene initiated by tetramethylammonium polymethylphenylsiloxane-α,ω-diolate, water causes an indication period that increases in length with higher water concentration [28]. The molecular weight of the polymer decreases and the reaction rate constant (k_{A_3}) calculated from the first order equation for the kinetic portion of the curves decreases.

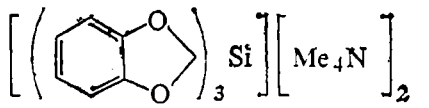
A reaction mechanism scheme was proposed to explain the influence that water had on the polymerization kinetics. This mechanism suggests that at the initial stage of the process slightly active complexes of silanolate groups are formed by the initiator with water molecules (C), and they greatly reduce the activity of these groups and this causes the induction period. The ability of tetramethylammonium polydiorganylsiloxane-α,ω-diolates to complex with water has been corroborated by the formation of a low-activity complex, $Me_2Si(ONMe_4)_2 \cdot 8H_2O$, when D_3 reacts with aqueous tetramethylammonium hydroxide [25]. In the course of the reaction, complex C interacts with A_3 to give siloxanols and liberate the siloxanolate end group which then raises the polymerization rate. Presumably, the siloxanol groups also favour a decrease in the activity of the siloxanolate groups through the formation of associations, but to a lesser extent than water. An analysis of this mechanism under quasistationary conditions (with respect to intermediate products), making allowance for the water concentration introduced together with the reactants ($[H_2O]_n$) and independently of them ($[H_2O]_x$) gives the dependence of k_{A_3} on the amount of water participating in the reaction:

$$1/k_{A_3} = 2K_e k_1^{-1} [H_2O]_x + 2K_p k_1^{-1} [H_2O]_n + k_1^{-1} = 2K_e k_1^{-1} [H_2O]_x + C \qquad (9)$$

where K_e is the equilibrium constant for the association reaction of the siloxanolate groups with the siloxanol ones and k_1 is the A_3 polymerization rate constant in the absence of water.

Experimental evidence agrees well with this equation.

It also follows from the suggested mechanism that the role of the condensation reaction of the silanol groups becomes more important at the end of the polymerization process, at deep conversions of A_3. This statement agrees with the data obtained by polymerization of D_3 initiated by



in the presence of water [29]. It shows that the concentration of the siloxanol groups at the end of the process decreases.

The terminal siloxanol groups take an active part in the polymerization reaction. This is indicated by a decrease in the molecular weight of the polymer at higher concentrations of water. The siloxanol groups participate in the process by engaging in a rapid proton-cation exchange. This was detected by the ^1H and ^{13}C NMR methods in a triorganylsilanol-sodium triorganylsilanolate system and follows this scheme [30-32]:

$$R^1R^2R^3SiOH + R^1R^2R^3Si^*ONa \underset{}{\overset{K_e}{\rightleftarrows}} R^1R^2R^3SiONa + R^1R^2R^3Si^*OH \qquad (10)$$

$R^1R^2R^3 = Me_3$, Me_2Ph, $MePh_2$, Et_3

Owing to the proton-cation exchange reaction between the siloxanol and siloxanolate groups, diorganylsiloxane-α,ω-diols periodically turn into active polymer chains. Since the exchange rate greatly exceeds the rate of polymerization, the probability of the growth of all chains is identical.

In D_4 polymerization initiated by methyltripropylphosphonium polymethylphenylsiloxane-α,ω-diolate (III), an increase in the number of growing polymer chains is observed at D_4 conversion degrees up to 20%; this number remains constant at conversion degrees ranging between 20 and 70%, but it is several times larger than should be expected on the basis of the initiator concentration. The appearance of an extra number of growing chains is caused by traces of water introduced into the reaction with the initiator, D_4 or desorbed from the walls of the reaction vessel. Molecules with siloxanol end groups are formed here; the molecules take an active part in the polymerization process through a rapid proton-cation exchange. III is also an active initiator of *cis*-A_3, *trans*-A_3 polymerization, their mixture, and of copolymerization of A_3 with D_4 [33].

The impurities of water and siloxanol end groups actively participate in thermal transformations of linear polydiorganylsiloxane with tetraorganylammonium or -phosphonium end groups. Thus, η_{sp} of polymethylphenylsilaxanes with different silanolate end groups (R_4M = Me_4N, Et_4N, Bu_4N, $Me_3(PhCH_2)N$, $MePr_3P$ and η_{sp} =

= 1.75, 1.62, 1.90, 1.84, 1.45, respectively) grows when heating at a 1 torr vacuum and 160 °C for 6 h to 2.76, 2.44, 3.09, 2.09, and 2.06, respectively. When heating at atmospheric pressure and at 200 °C for 5 min, η_{sp} drops (to 0.90, 1.33, 1.13, 1.07, 0.96, respectively). The decrease of viscosity in the latter case is caused by the breakdown of the polymer chain in the presence of a nucleophilic initiator and water traces with the formation of shorter chains with siloxanol end groups. Viscosity increase when heating the polymers in vacuum is due to a shift of the condensation reaction of the siloxanol groups towards forming the $\equiv SiO—Si\equiv$ bond and the growth of the polymer's molecular weight through water removal [27].

The existence of a rapid proton-cation exchange was an incentive to study the influence of hydroxyl-containing compounds on the catalytic activity of initiators of the anionic polymerization of OCS.

The effect of silanols on the catalytic activity of sodium trimethylsilanolate was examined in D_3 polymerization in the presence of trimethylsilanol (TMS) in a toluene solution at 40-80 °C [34]. Under these conditions, the reaction is not at equilibrium. This is suggested by the absence of higher cyclodimethylsiloxanes in its products.

During D_3 polymerization at 80 °C in the absence of Me_3SiOH and at different concentrations of Me_3SiONa (from 0.05 to 0.20 mol/litre), the reaction rate is first order with respect to the current concentration of D_3.

$$W_{D_3} = -k_{D_3}[D_3] \tag{11}$$

The k_{D_3} values grow in proportion to $[ONa]_0$, thus indicating that they are first order with respect to the initiator.

$$W_{D_3} = -k^1_{D_3}[D_3][ONa]_0 \tag{12}$$

These data diverge greatly from those obtained from the equilibrium polymerization of OCS by alkali silanolates and hydroxides. The order was 0.5 with respect to the initiator [3]. This is evidently caused by the non-equilibrium character of the reaction and by the self-association propensity of sodium trimethylsilanolate.

X-Ray structure analysis [35] shows that the crystalline product of a reaction between Me_3SiOH and metallic sodium is composed of globular associations with a $10Me_3SiONa \cdot NaOH$ composition. The sodium cations, having a coordination number of 3 or 4 in the association instead of 6, which is peculiar to them, are coordination-unsaturated. The Me_3SiONa associations are stable in diluted solutions. According to H. Schmidbaur et al. [36], the molecular weight of sodium trimethylsilanolate in dilute solutions indicates the presence of a decamer. It can therefore be suggested that sodium trimethylsilanolate participates in the form of an association in the D_3 polymerization reaction as follows:

$$10Me_3SiONa \cdot NaOH + n[Me_2SiO]_3 \rightarrow 9Me_3SiONa \cdot NaO[Me_2SiO]_{3n}SiMe_3 \tag{13}$$

All the molecules of Me_3SiONa and NaOH are progressively consumed to give sodium polydimethylsiloxanolate. This in turn causes the polymerization of D_3 also in the associated form, as the degree of association is less than that of sodium trimethylsilanolate [37].

In the presence of Me_3SiOH, as in its absence, the reaction rate is first order with respect to D_3; however, the activity of the initiator increases raising k_{D_3} by more than a factor of 30 and the $[Me_3SiOH]_0/[ONa]_0$ ratio (α) from 0 to 15. The general character of k_{D_3} variation with the increase of α remains unchanged with the reaction temperature growing from 40 to 80 °C. The dependence of k_{D_3} on α also leads to a situation when the growth of $[ONa]_0$ at a constant $[Me_3SiOH]_0$ causes the reaction order to be less than unity with respect to the catalyst. Thus, at $[D_3]_0 = 1.5$ mol/litre, $[Me_3SiOH]_0 = 0.4$ mol/litre and $[ONa]_0$ varying from 0.05 to 0.20 mol/litre, the order with respect to the catalyst is 0.4 ± 0.1. At $\alpha > 15$, the dependence of k_{D_3} on α is not significant, and the observed order with respect to the catalyst should be close to unity.

When α grew from 0 to 15, E_{act} and A_0 in the Arrhenius equation also grew from 62 to 78 kJ/mol and from 6.7×10^5 to 5.7×10^9 s^{-1}, respectively $\Delta H^{\neq}$ grows from 59 ± 7 to 75 ± 8 kJ/mol and $\Delta S^{\neq}$ from -142 ± 16 to -67 ± 8 J/mol·deg for the transition state calculated from the Eyring equation. This indicates the destruction of the sodium trimethylsilanolate associations in the presence of Me_3SiOH with the formation of more simple associations of trimethylsilanol with sodium trimethylsilanolate. This event is also accompanied by a decrease in the ionicity of the ≡Si—O—Na bond. The increase of the initiator activity is caused by weakening of steric hindrances to the formation of a transition complex during the decomposition of the self-associated clusters. This increase surpasses a certain decrease of the activity due to the drop of the ionicity of the ≡Si—O—Na bond.

These findings agree with the results of studies of crystalline hydrates formed in the Me_3SiONa-Me_3SiOH system during long stay. Their composition depends on the α value. Thus, at $\alpha = 10$, the crystalline hydrate of a $Me_3SiONa \cdot 4H_2O$ composition was isolated within 400 h; at $\alpha = 5$, $Me_3SiONa \cdot 3H_2O$ within 72 h; at $\alpha = 1$, $Me_3SiONa \cdot 3NaOH \cdot H_2O$ within 400 h.

According to X-ray analysis, the crystals of $Me_3SiONa \cdot 3H_2O$ are composed of double hydrophobic layers consisting of methyl groups and of hydrophilic layers that include silanolate groups and water molecules [38]. The oxygen atoms of the siloxy groups and water are linked together by coordination bonds through sodium cations and the protons of water. This weakens the ionicity of the ≡Si—O—Na bond and increases its length (from 1.58 to 1.617 Å) as it goes from $10Me_3SiONa \cdot NaOH$ to $Me_3SiONa \cdot 3H_2O$. The destruction of

the self-associated clusters of sodium trimethylsilanolate during their interaction with trimethylsilanol is favoured by rapid proton-cation exchange.

The influence of Me_3SiOH on the activity of tetramethylammonium polydimethylsiloxane-α,ω-diolate (TMAS) was studied on an example of the polymerization of D_3 in toluene at 25-60 °C [39-42]. Under these conditions the reaction is not at equilibrium. At $[Me_3SiOH]_0 < < [D_3]_0$, the reactants are quantitatively consumed

$$W_{D_3} = -k_{D_3}[D_3] \tag{14}$$

and $$W_{TMS} = k_{TMS}[TMS] \tag{15}$$

The initial rate of the consumption of Me_3SiOH is equal to the initial rate of the transformation of D_3. This indicates that the preferred interaction is between Me_3SiOH and D_3. The values of k_{D_3} and k_{TMS} remain constant in the course of the reaction but decrease at higher $[Me_3SiOH]_0/[NMe_4]_0 = \alpha$ ratios. The k_{D_3} value drops abruptly when α is changed from 0 to 50 but at higher α values it varies insignificantly. It was found that at constant $[Me_3SiOH]_0$ and different $[NMe_4]_0$, the k_{D_3} value grows faster than $[NMe_4]_0$ if $\alpha < 50$, and at $\alpha \geqslant 50$ or in the absence of Me_3SiOH is directly proportional to $[NMe_4]_0$.

When α grows from 0 to 500, E_{act} decreases from 124 to 40 kJ/mol, and A_0, to 2×10^3 s^{-1} from 1.7×10^{18} s^{-1}; the values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ also diminish from 121 ± 11 kJ/mol and 102 ± 11 J/mol·deg to 37 ± 4 kJ/mol and -190 ± 20 J/mol·deg. It follows from this that the nucleophility of the siloxanolate groups in the initiator increases during their solvation with the silanol groups of Me_3SiOH. This is because of antibonding in the $Me_4\overset{+}{N}O\overset{-}{S}iMe_2O-$ ion pair and that the steric hindrances to the formation of the transition complex become more pronounced. The decrease in the initiator activity which results from the enhancement of the steric hindrances to the transition complex formation surpasses its growth caused by the antibonding of the ion pair.

If $[Me_3SiOH]_0 > [D_3]_0$, then the homocondensation of Me_3SiOH proceeds together with the interaction of D_3 with trimethylsilanol and the cocondensation of Me_3SiOH with siloxanols formed in the course of the reaction. The rate of cocondensation is much less than that of D_3 interacting with Me_3SiOH, but higher than the rate of trimethylsilanol homocondensation.

The first order with respect to Me_3SiOH and the initiator

$$W_{TMS} = -k^{I}_{TMS}[TMS][NMe_4]_0 \tag{16}$$

in Me_3SiOH homocondensation and the decrease of k^{I}_{TMS} at higher $[Me_3SiOH]_0$ suggest that trimethylsilanol and water formed during

the reaction solvate the catalyst and form associations whose transformations are the rate-limiting stage [43].

The fact that the consumption of D_3 and Me_3SiOH is first order during D_3 polymerization initiated by Me_3SiONa or tetramethylammonium polydimethylsiloxane-α,ω-diolate in the presence of Me_3SiOH indicates that the slowest stage of the process is the interaction of the initial reagents with the solvated reaction sites of the initiator. As a result of proton-cation exchange, the system contains two fundamental types of catalytic particles based on trimethylsilanolates and polydimethylsiloxane-α,ω-diolates:

$$\underset{\text{IV}}{OMe_2SiOM(HOSiMe_3)_n} \cdot (HOSiMe_2)_m \rightleftarrows \underset{\text{V}}{Me_3SiOM \cdot (HOSiMe_3)_{n-1}} \cdot (HOSiMeO_2)_{m+1} \quad (17)$$

$M = Na;\ Me_4$

Trimethylsilanol is consumed in the course of ligand exchange with the associations IV and V accompanied by displacement of the polydimethylsiloxanols and further transformations in the associations:

$$IV + HOSiMe_3 \rightleftarrows {\sim}OMe_2SiOH + {\sim}OMe_2SiOM \cdot (HOSiMe_3)_{n+1} \cdot (HOSiMe_2O)_{m-1} \quad (18)$$

$$V + HOSiMe_3 \rightleftarrows Me_3SiOM \cdot (HOSiMe_3)_n \cdot (HOSiMe_2O)_m + HOSiMe_2O{\sim} \quad (19)$$

D_3 is consumed on interacting with associations IV and V:

$$V + [Me_2SiO]_3 \rightleftarrows Me_3Si(OSiMe_2)_3OM \cdot \underset{\text{IV}}{(HOSiMe_3)_{n-1}} \cdot (HOSiMe_2O)_{m+1} \quad (20)$$

$$IV + [Me_2SiO]_3 \rightarrow \underset{\text{IV}}{(OMe_2Si)_4OM \cdot (HOSiMe_3)_n} \cdot (HOSiMe_3)_n \cdot (HOSiMe_2O)_m \quad (21)$$

The constancy of k_{D_3} during the reaction and its variation as α grows indicates that the activity of the reaction sites changes only slightly in going from Me_3SiOH and trimethylsilanolates which are present mostly at the beginning of the process to polydimethylsiloxanolates and polydimethylsiloxanols at the end; it depends only on the degree of their solvation by silanol groups.

If the reaction is initiated by nucleophilic reagents, aliphatic alcohols, unlike water and Me_3SiOH, less strongly affect the rate at which OCS polymerizes and the composition of the reaction products [44]. Thus, when D_3 polymerization is initiated by tetramethylammonium polydimethylsiloxane-α,ω-diolate in the presence of PrOH and BuOH (at concentrations one order of magnitude lower than the concentration of D_3), the k_{D_3} value decreases to about 1/3 of the initial level. At the same time, when in the presence of the same amounts of Me_3SiOH, k_{D_3} drops to less than 1/30. This is ap-

parently a result of the weaker complexing ability of these alcohols, and of the shift of the proton-cation exchange reaction between the alcohols and the siloxanolate towards the formation of the latter.

The proton-cation exchange reaction favours the active interaction between OCS and aliphatic diols in the presence of anionic initiators. Thus, during A_3 (a mixture of *cis* and *trans* isomers) polymerization initiated by potassium trimethyltriphenylsiloxane-1,5-diolate (VI) in the presence of equimolar amounts of diethylene glycol (DEG), both reactants are completely engaged in the reaction. Examination of the kinetics of this reaction in toluene at 60 °C (under conditions precluding the formation of water) showed that up to 70% conversion the rate of A_3 consumption is first order with respect to the cycle and the initiator

$$W_{A_3} = -k^{I}_{A_3}[A_3][VI]_0 \qquad (22)$$

In boiling toluene, the reaction is accompanied by the liberation of water. This is caused by condensation of siloxanol groups formed during the interaction between A_3 and DEG [45, 46].

The rate of the liberation of water when DEG reacts with different OCS (A_3, D_3, D_4, $(MeVinSiO)_4$) in the presence of various amounts of initiator VI and KOH is determined by the nature of the organic substituents at the silicon and by the ratio between the concentrations of the initial reactants.

Copolymerization of polydiorganylsiloxane-α,ω-diols with OCS was used for preparing siloxane block copolymers [47]:

$$p\,HO\{R^1_2SiO\}_n H + pm[R^2R^3SiO]_3 \xrightarrow{R_4NO[SiMePhO]_nRN_4}$$

$$\longrightarrow OH\{(R^1_2SiO)_n(R^2R^3SiO)_{3m-p}\}H + (2p-1)H_2O \qquad (23)$$

R^1 = Me; R^2R^3 = MePh, MeVin, $Me(CF_3CH_2CH_2)$; R = Me_3Ph

The effect of water on the process of amine-initiated anionic polymerization of OCS was studied in A_3 polymerization in the presence of piperidine or its equimolar mixture with water [48]. In the latter case the reaction rate is 1-2 orders of magnitude higher than with anhydrous piperidine. The reaction is first order with respect to A_3 and, in the absence of water, to piperidine as well

$$W_{A_3} = -k^{I}_{A_3}[A_3]\cdot[Amine]_0 \qquad (24)$$

When a mixture of piperidine with water is used, the reaction is second overall order with respect to piperidine and water

$$W_{A_3} = -k^{II}_{A_3}[A_3][Amine]_0[H_2O]_0 \qquad (25)$$

In the presence of water, the molecular weight of the polymerization products decreases at higher concentrations of water. This testifies to its participation in the reaction. Polymerization is initiated by the am-

monium base formed as a result of piperidine interacting with water, and by siloxanolate ammonium groups which are the products of the reaction of the ammonium base with A_3. After water has entered the reaction, polymerization is run by the corresponding siloxanolates.

The processes initiated by the fluorine anion are a new type of OCS polymerization [49, 50]. When ionizable fluorides are employed, the activity of F^- decreases in a series:

$$Me_4NF = Bu_4NF \cdot 2H_2O > KF > NaF$$

NaF does not induce the polymerization of OCS, and KF polymerizes only A_3 at 100 °C. On the other hand, Me_4NF and $Bu_4NF \cdot 2H_2O$ initiate the polymerization of A_3, D_3, and D_4. The addition of an ionizing solvent substantially raises the reaction rate. In Me_4NF-initiated polymerization of D_4 in the presence of 4.7% DMFA, the reaction is first order with respect to the cycle and second order with respect to the initiator.

The addition of Me_3SiOH greatly increases the rate of D_3 polymerization initiated by Me_4NF. However, depending on the $[Me_3SiOH]_0/[Me_4NF]_0 = \alpha$ ratio, the polymerization rate constant passes through a maximum. This phenomenon is due to the features of the effect of Me_3SiOH on different stages of the D_3 polymerization. This involves the reversible process of fluoride reacting with D_3 giving rise to terminal fluorosilyl and siloxanolate groups, the polymerization of D_3 induced by the formed siloxanolates, and the condensation of siloxanolate and fluorosilyl end groups.

Active initiators of the anionic polymerization of OCS are compounds of graphite (LGC) laminated with potassium or lithium (LGC-K or LGC-Li) [51-55]. The polymerization of D_3, D_4, A_3 initiated by LGC-K gives polymer yields in approximately equilibrium values. In the presence of LGC-K, D_4 and A_3 form polymers with m.w. 4.5×10^5-5.5×10^5. The cycle/initiator (on conversion to potassium) molar ratio exerts no significant influence on the m.w. and the final yield of the polymer. D_3 is polymerized with the formation of a high-molecular product, if the D_3/K (in LGC) ratio is not less than 1:900 (83% yield, m.w. 4.0×10^5). LGC-Li do not catalyze the polymerization of D_4 at temperatures up to 160 °C either in block or in polar solvent. However, D_3 forms a polymer in THF after 7 h at 20 °C (94% yield, 2.03×10^5 m.w.). The polymerization of $[Me(CF_3CH_2CH_2)SiO]_3$ on LGC-Li at 160 °C gives a polymer with m.w. 9.6×10^5 within 5.5 h. Deactivated (with trimethylchlorosilane) and non-deactivated (the initiator is filtered off) polymers retain their characteristics after prolonged boiling in dilute toluene solution. To all appearances, potassium or lithium is present in the polymer but in so negligible amounts that they have no destructurizing effect on it. The data provided by X-ray

fluorescence analysis show that a non-reprecipitated polymer (m.w. 5.4×10^5) prepared by LGC-K-initiated D_4 polymerization contains potassium in a concentration which is 2 orders of magnitude less (below 1×10^{-4} wt. %) than the polymer with the ≡Si—O—K end groups should contain.

Since in LGC-initiated polymerization of OCS, the impurities blocking and terminating the chain are not present in the system, it can be suggested that the macromolecules formed have a cyclic structure. LGC-initiated OCS polymerization seems to involve the breakdown of the endocyclic siloxane bond with the formation of a dianion and the transfer of electrons from the carbon network of graphite to the OCS adsorbed on it, the graphite network acting as a counterion. The chain grows by the OCS penetrating into the bond between the anion and the carbon network of graphite, and is terminated by a reaction in the chain accompanied by the formation of cyclic polydiorganylsiloxane and its withdrawal from the graphite surface. If water is present in the system, LGC will interact with water to give hydroxides which polymerize OCS by the ordinary mechanism.

In conclusion, it should be noted that ionic polymerization of OCS is a complicated process whose course depends not only on the cycle size, the nature of the substituents at the silicon atom, and in the initiator, but also on the proton-donor agents present in the reaction medium. The data reviewed here indicate that the character of interaction of the proton-donor agents with the initiator strongly affects the polymerization process, and the composition and structure of the polymers obtained.

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6 High-temperature Synthesis of New Silicon-containing Heterocyclic Systems

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The present authors have developed original high-temperature syntheses of new silicon-containing heterocyclic systems based on the reaction of thermal cyclization in the gaseous phase. They open straightforward and efficient ways to synthesize the numerous earlier unavailable classes of heterocyclic compounds with one or two silicon atoms in the ring.

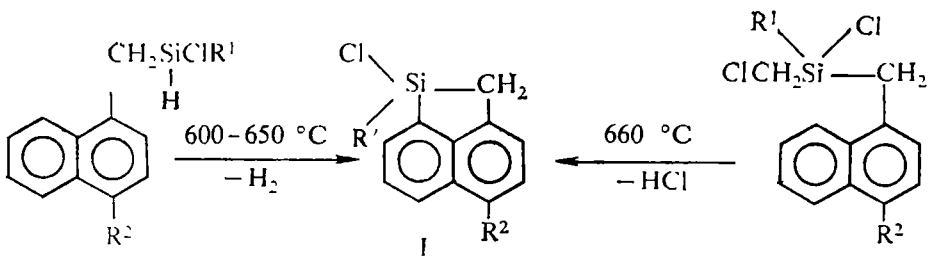
The development of directed pyrolytic processes as applied to the chemistry of organosilicon compounds is an important and interesting problem. Elaboration of a generally applicable method to generate a Si—C bond, known as "the high-temperature condensation method", has contributed appreciably to the solution of the problem referred to above. The method relies on a gas-phase thermal interaction in a flow-type system between chloro- or organylchlorohydrosilanes and the chlorine derivatives of aromatic and unsaturated hydrocarbons [1, 2]. The high-temperature condensation technique has not only turned a new page in the synthetic chemistry of organosilicon monomers but also has furnished a foundation for their commercial production. Further development of the above technique has led to the synthesis of the new classes of heterocyclic systems whose preparation seemed unreal not long ago. Although the potentialities of pyrolytic cyclization are far from being exhausted, one can even now formulate the basic ways of synthesizing these heterocyclic systems. These include the thermal intramolecular cyclization of organosilicon compounds containing structural fragments essential for cyclization, a two-component copyrolysis of a variety of organic and organosilicon compounds in the presence of trichlorosilane, organylchlorohydrosilanes, and perchloropolysilanes, as well as thermal cyclization of arylchlorosilanes in the presence of halogenated alkanes and alkenes.

1. THERMAL INTRAMOLECULAR CYCLIZATION

The vast bulk of experimental evidence has been accumulated to date, which makes it possible to utilize gas-phase intramolecular cyclization for a directed synthesis of silicon-functional heterocyclic systems. Basic principles have been devised for such

reactions to be carried out. This primarily involves the presence in a starting compound of thermally labile bonds and bonds possessing greater reactivity due to the spatial interaction with bulky substituents (in the α-substituted derivatives of naphthalene and in the *ortho*-substituted derivatives of diphenyl and benzene). The above reactions proceed to eliminate hydrogen, hydrogen chloride, methane, benzene, or naphthalene.

The greater reactivity of the *peri*-hydrogen in the α-substituted derivatives of naphthalene having a structural fragment required for cyclization, both with a thermally readily cleavable Si—H bond and a C_{alk}—Cl bond, has enabled several reactions to proceed thereby leading to a novel tricyclic structure, 1,1-dichloro-1-silaacenaphthene and its derivatives (I) [3-5]:



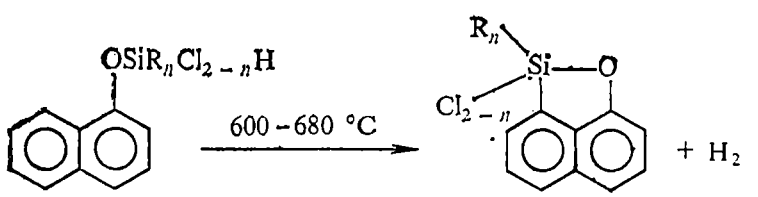
(1)

I

$R^1 = Cl, CH_3$; $R^2 = H, CH_3$

Under the conditions of thermal silicoalkylation, the yields of heterocycles amount to 30%, whereas on dehydrocyclization, they exceed 50%.

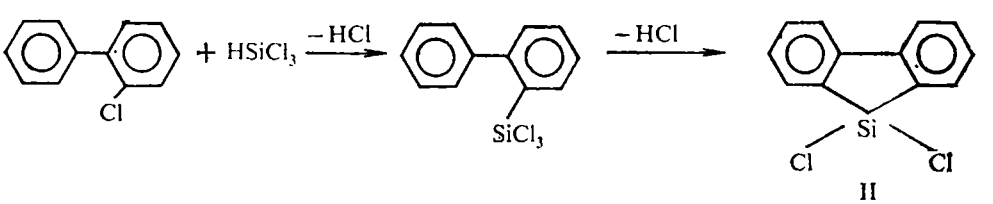
The common character of the reaction detected was illustrated for pyrolysis of α-naphthoxychlorohydrosilanes [6]:



(2)

R = Cl, alkyl, aryl; $n = 0, 1$ (60%)

Pyrolysis of *o*-substituted diphenyls has proved a fairly fruitful synthesis of silicon-containing heterocycles. The reaction between *o*-chlorodiphenyl and trichlorosilane at 650-690 °C yields *o*-trichlorosilyldiphenyl, which undergoes intramolecular cyclization to convert to 9,9-dichloro-9-silafluorene (II) in a greater than 50% yield [7, 8].

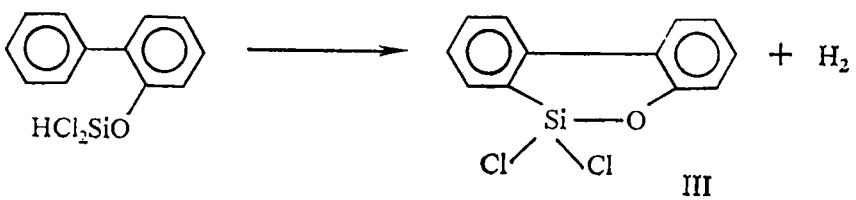


(3)

II

This reaction has provided the first example of silylation proceeding in such high yields and breaking the Si—Cl bond for which such type of reaction is not characteristic. The reaction between *o*-chlorodiphenyl and methyldichlorosilane likewise leads to the formation of II, that is, in this case an energetically weaker Si—CH_3 bond breaks.

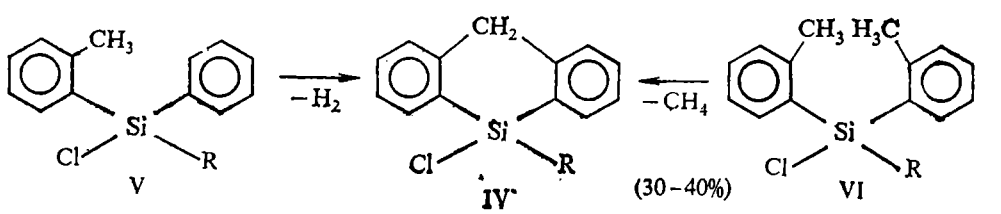
A heterocycle having a phenanthrene skeleton with a Si—O fragment inserted at position 9,10 has been synthesized from *o*-oxydiphenyl in high yields. Initially, 10,10-dichloro-9-oxa-10-sila-9,10-dehydrophenanthrene (III) was produced in yields of about 60% by a gas-phase pyrolysis of *o*-dichlorosiloxydiphenyl [9, 10]:



III (4)

The intramolecular cyclization of *o*-siloxysubstituted derivatives of diphenyl also occurs when the silicon along with chlorine and hydrogen contains a phenyl or methyl radical. Si-substituted *o*-oxydiphenyls can undergo cyclization not only via the Si—H bond but also via other bonds at the silicon, yet the heterocycles are prepared in by far lower yields. Pyrolysis of *o*-trimethylsiloxydiphenyl leads, for instance, to 10,10-dimethyl-9-oxa-10-sila-9,10-dehydrophenanthrene in as small as 5% yield. Cyclization of *o*-trichlorosiloxydiphenyl via the Si—Cl and C_{ar}—H bonds occurs in higher yields (30%).

Cyclization involving hydrogen elimination can also occur without participation of the bond at the silicon. For example, the presence of a methyl group at the *o*-position of the phenyl ring of diphenyldichlorosilane allows cyclization via C—H bonds [11, 12]. Formation of the Si-chlorine-substituted derivatives of 9-sila-9,10-dihydroanthracene (IV) is also promoted by a spatial effect from the two methyl groups being brought together in a molecule of bis(2-methylphenyl)dichlorosilane [12]:

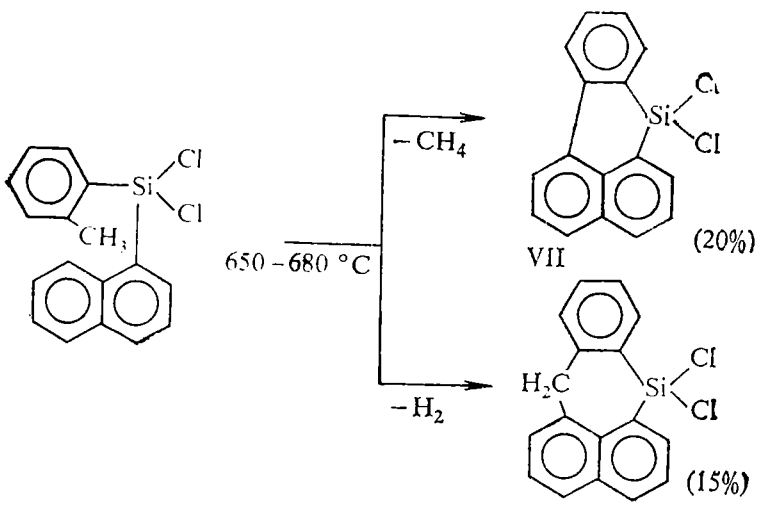


(5)

R = Cl, CH_3

The pyrolytic processes of compounds V and VI giving rise only to heterocycles with a skeleton of the 9,10-dihydroanthracene type exhibit certain directivity.

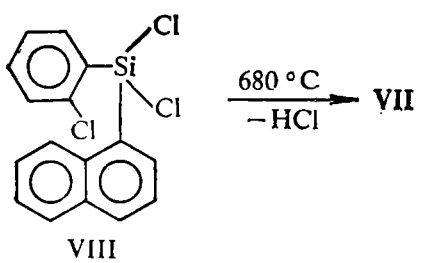
Such cyclization is also characteristic of *o*-tolyl(α-naphthyl)dichlorosilane. However the pyrolytic conversions of the latter are not as highly selective [13]:



(6)

The reaction proceeds to eliminate methane. This can be attributed to the tendency to undergo cyclization into a more stable six-membered heterocyclic structure.

The thermal intramolecular condensation of *o*-chlorophenylnaphthyldichlorosilane (VIII) was successfully employed to synthesize 1,1-dichloro-1-sila-2,3-benzophenalene (VII), the first representative of the new class of silicon-containing heterocycles [13, 14]:

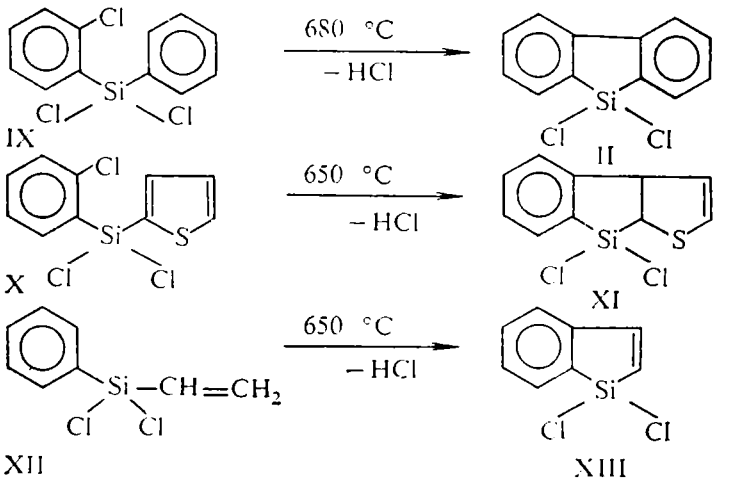


VIII

(7)

Investigation of pyrolysis of the *o*-chlorine-substituted derivatives of diphenyldichlorosilane, phenylthienyldichlorosilane, and phenylvinyldichlorosilane has corroborated the common character of the detected cyclization reaction which proceeds to eliminate hydrogen chloride and synthesize new heterocyclic systems having the silicon

atom in the ring [15-17]:

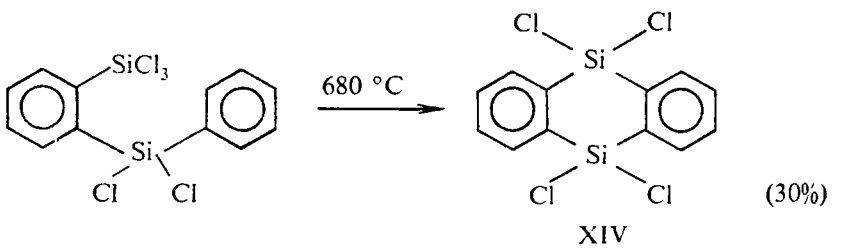


IX → II (15%) (8)

X → XI (10%) (9)

XII → XIII (10%) (10)

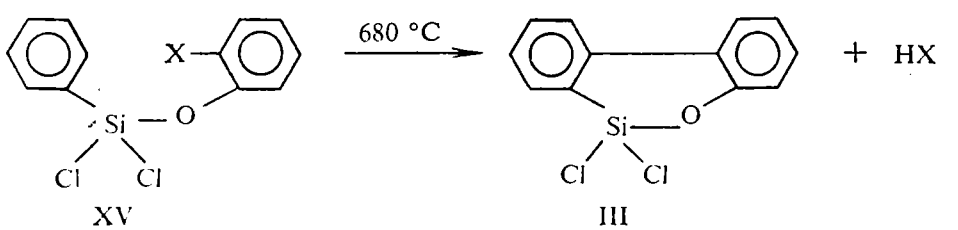
The presence of a more bulky trichlorosilyl group at the *o*-position of diphenyldichlorosilane facilitates intramolecular cyclization even at the expense of a thermally stable bond, such as Si—Cl [15]:



(11)

XIV (30%)

Employing the same principle of pyrolytic synthesis of silicon-containing heterocycles as in reactions (5) and (8) to (11), it is possible to cyclize several organosilicon compounds wherein two phenyl rings are separated by a Si—O fragment instead of one Si atom [18]:



(12)

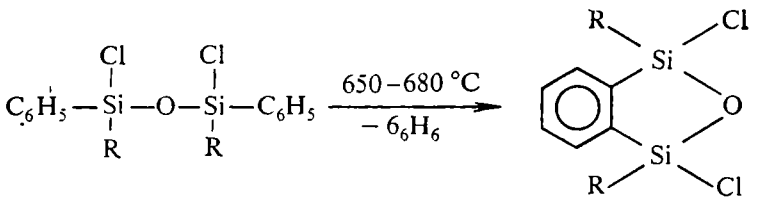
XV → III

X = Cl, Br, CH_3

In this case, however, the yields range merely from 5 to 15%.

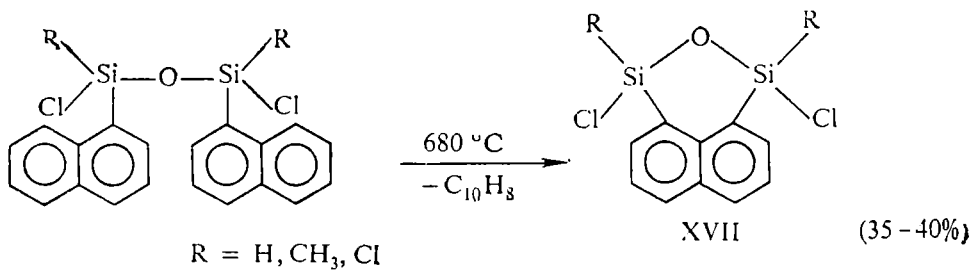
The pyrolytic conversions of Si-substituted 1,3-diaryldisiloxanes are of interest [19-21]. As an example, the cyclization of the derivatives of 1,3-diphenyl-1,3-dichlorodisiloxane involving elimination of a benzene molecule leads to Si-substituted 2-oxa-1,3-disilaindans

[19, 21]:



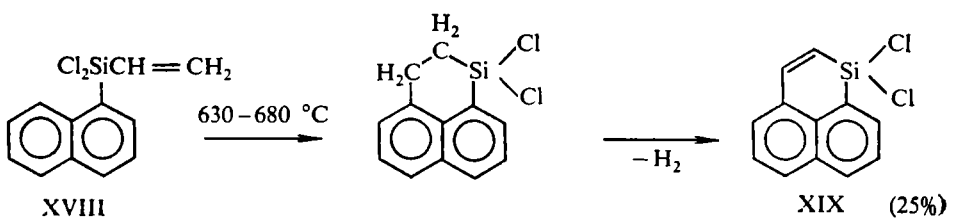
(13)

Pyrolysis of the derivatives of 1,3-di(α-naphthyl)disiloxane that proceeds to eliminate naphthalene is of preparative significance [20, 21]:

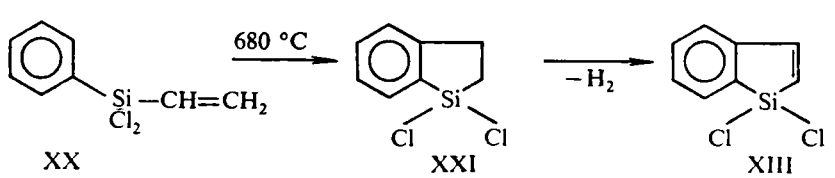


(14)

Here it is appropriate to report also the methods for preparing novel unsaturated aromatic silacarbocyclic compounds, 1,1-dichloro-1-silaphenalene (XIX) and 1,1-dichloro-1-silaindene (XIII), although hydrogen elimination on their synthesis is not essentially a primary process. These heterocyclic structures seem to form due to the thermal intramolecular alkylation of the corresponding organosilicon compounds followed by their thermal dehydrogenation into stable cyclic systems [17, 22, 23]:



(15)



Formation of XXI on pyrolysis of phenylvinyldichlorosilane and the ability of XXI to dehydrogenate, under the conditions indicated, into XIII have been confirmed through experiments.

2. SYNTHESIS OF SILICON-CONTAINING HETEROCYCLES BASED ON THE UNSTABLE DERIVATIVES OF BIVALENT SILICON

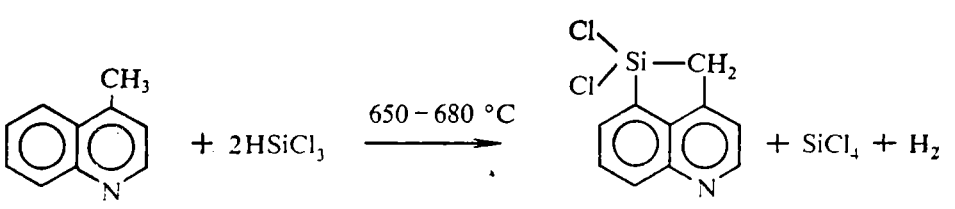
In recent years a great deal of attention has been given to the study into the chemistry of the unstable compounds of silicon, viz. silylenes. From the synthetic viewpoint, dichlorosilylene is of particular interest. Its utilization allows several applied problems to be solved including preparation of silicon-containing heterocyclic compounds [24, 25]. Trichlorosilane, hexachlorodisilane, and higher perchloropolysilanes serve as a source of $:SiCl_2$ in the gaseous phase.

2.1. Synthesis Using Trichlorosilane and Organylchlorohydrosilanes

Studies of the synthesis of organosilicon compounds by high-temperature condensation [4, 26] have led to the discovery of exotic cyclization in the reaction of α-methylnaphthalene with trichlorosilane, which gives rise to 1,1-dichloro-1-silaacenaphthene (I) ($R' = Cl$, $R^2 = H$) [4, 27]:

$$\alpha\text{-}CH_3C_{10}H_7 + 2HSiCl_3 \xrightarrow{650-680^\circ C} \underset{50\%}{I} + SiCl_4 + H_2 \qquad (16)$$

The considerable selectivity of reaction (16), the high yield of I, and the availability of the starting reactants promoted the development of the high-temperature synthesis of silicon-containing heterocyclic systems using trichlorosilane. Reactions similar to (16) implicated a variety of methyl-substituted naphthalenes and quinolines [27-29]. By way of example, the thermal reaction between 4-methylquinoline and trichlorosilane synthesized 1,1-dichloro-1-sila-5-asaacenaphthene, the first representative of a polynuclear heterocyclic system including the silicon and nitrogen [28-29]:



XXII (35%) (17)

These reactions appear to proceed via insertion of dichlorosilylene formed from trichlorosilane into the C—H bond of a methyl substituent followed by the intramolecular dehydrocyclization of α-dichlorosilylmethyl-substituted naphthalene (XXIII) or quinoline, for example:

(18)

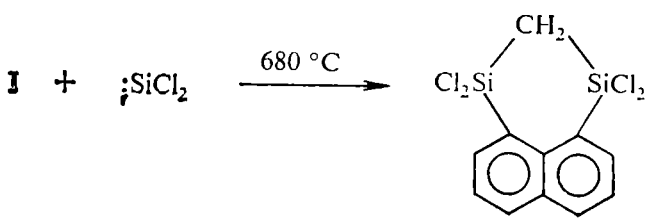
XXIII

It has been possible to isolate these compounds from the reaction mixture, although in minor yields (as low as 5%). The fact that $:SiCl_2$ is likely to participate in thermal processes using trichlorosilane is borne out by kinetic studies and thermodynamic calculations [30-33]. To illustrate, silicon tetrachloride, hydrogen, and silicon are the main products of the high-temperature decomposition of trichlorosilane [30-32]. Kinetic evidence indicates that $:SiCl_2$ is an intermediate product of $HSiCl_3$ pyrolysis:

$$2HSiCl_3 \rightarrow SiCl_4 + H_2 + :SiCl_2 \qquad (19)$$

Moreover, thermodynamic calculations demonstrate that the amount of dichlorosilylene in an equilibrium mixture is as high as 5-8% [33].

A theoretical possibility to expand the five-membered ring of a heterocycle into a six-membered species containing two silicons [25, 33] was first shown for the thermal reaction of I ($R' = Cl$, $R^2 = H$) with trichlorosilane or benzyldichlorosilane which is also a source of dichlorosilylene [25, 33]:



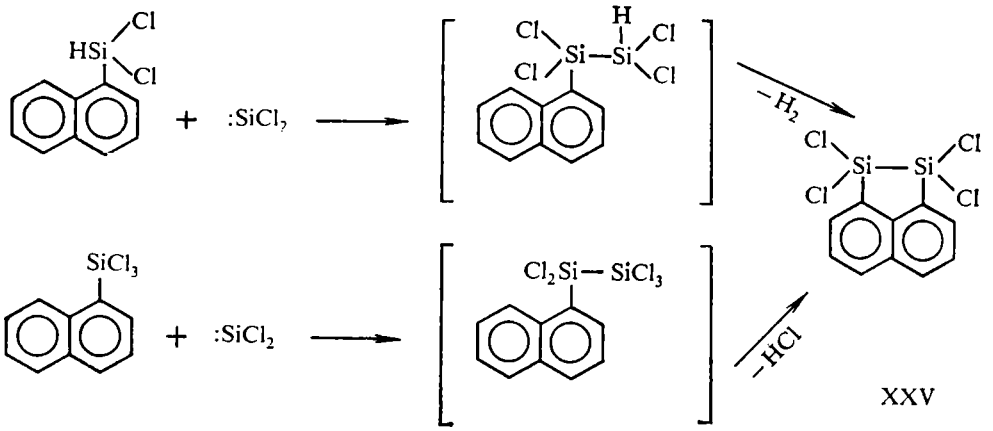
(20)

XXIV

Formally the formation of 1,1,3,3-tetrachloro-1,3-disilaphenalane (XXIV) can be envisioned as insertion of $:SiCl_2$ into the C_{ar}—C bond.

Production of 1,1,2,2-tetrachloro-1,2-disilaacenaphthene (XXV), which is a heterocyclic system with a fairly stable endocyclic Si—Si bond, via a gas-phase pyrolysis of α-naphthyldichlorosilane or α-naphthyltrichlorosilane in a mixture with trichlorosilane is extremely interesting from the synthetic viewpoint [2, 25, 33]. In this case

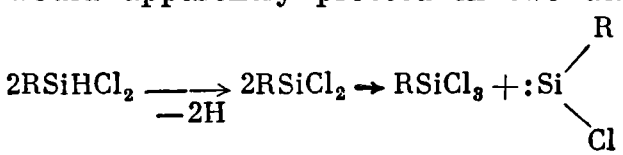
the reaction occurs via insertion of dichlorosilylene into the Si—H bond and even into the Si—Cl bond of the corresponding α-naphthylchlorosilanes:



(21)

XXV

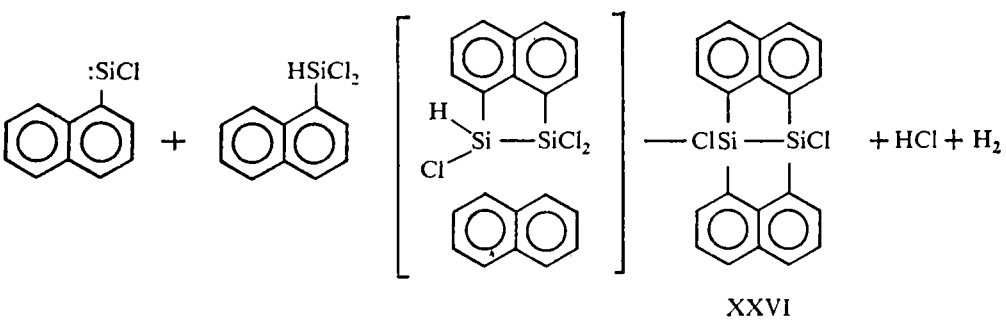
Both dichlorosilylene and other carbenoid particles, such as organylchlorosilylenes which are likely to be donated by some organylchlorohydrosilanes (α-naphthyldichlorosilane, phenyldichlorosilane, methyldichlorosilane) have been found to be of major importance in the high-temperature reactions of the formation of silicon-containing heterocycles [2, 25, 34, 35]. Their thermal decomposition would apparently proceed in two directions:



(22)

$RSiHCl_2 \rightarrow RH + :SiCl_2$

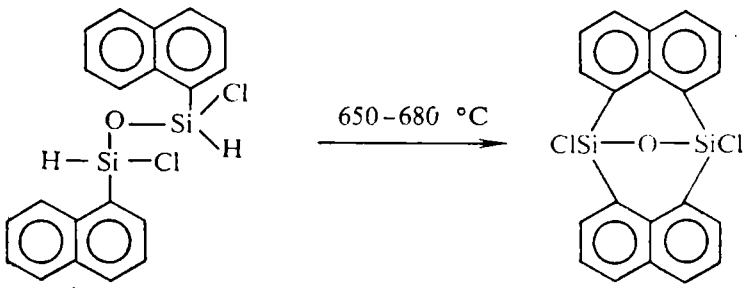
By way of example, gas-phase pyrolysis of α-naphthyldichlorosilane results in two heterocyclic compounds with an endocyclic bond, silicon-silicon (XXV) and bis(1,8-naphthylene)dichlorodisilane (XXVI) [34, 35]. The carbenoid scheme of formation of XXVI, which suggests insertion of an intermediate α-naphthylchlorosilylene into the Si—H bond of the starting α-naphthyldichlorosilane, seems to be the most likely:



(23)

XXVI

The intermediate product of insertion can undergo cyclization. This was confirmed by synthesis of bis(1,8-naphthylene)-1,3-dichlorodisiloxane (XXVII) through an intramolecular cyclization of the corresponding symmetrical disiloxane [21, 36]:

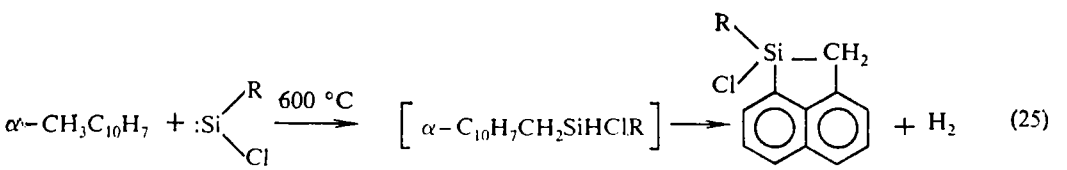


(24)

XXVII

The high-temperature synthetic method has produced silicon-containing heterocyclic systems XXVI and XXVII, which have no hydrocarbon analogues.

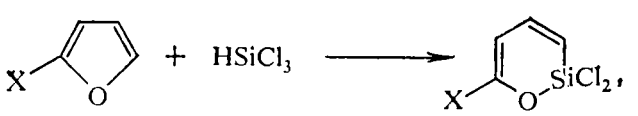
Studies of the thermal reaction between α-methylnaphthalene and phenyl- or methyldichlorosilane have shown that siliconmonofunctional heterocycles, such as 1-phenyl (or 1-methyl)-1-chloro-1-silaacenaphthene, can likewise be synthesized [21, 25]:



(25)

R = C_6H_5, CH_3 XXVIII

Silicon-containing heterocycles can be produced not only by cyclization but also by expanding certain cyclic systems [37-39]. For example, the gas-phase thermal reaction of furan and its α-substituted derivatives with trichlorosilane yields the derivatives of 2,2-dichloro-1-oxa-2-sila-1,2-dihydrobenzenes (XXIX):

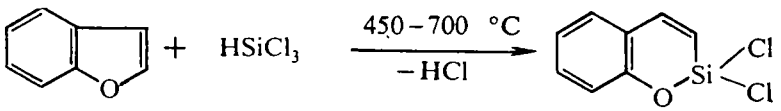


X = H, CH_3, C_6H_5 (26)

XXIX

Its yield is as high as 50%.

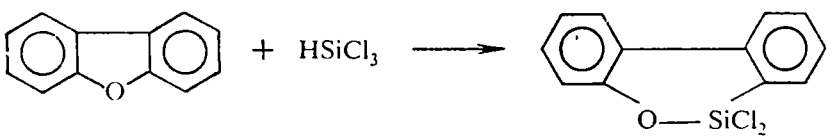
Trichlorosilane reacts more readily with benzofuran to form 2,2-dichloro-1-oxa-2-sila-1,2-dihydronaphthalene (XXX):



(27)

XXX

The highest yield of XXX (70%) was obtained at 640 °C and a 1:2 molar ratio between benzofuran and trichlorosilane. Under similar conditions, dibenzofuran gave compound III in good yield:



(28)

III

Thus, utilization of trichlorosilane and organylchlorohydrosilanes as sources of dichloro- or organylchlorosilylenes with a view to synthesizing silicon-containing heterocycles has proved remarkably productive. The $:SiCl_2$ generated from trichlorosilane can be used to prepare silicon-containing heterocycles in the gas-phase reactions of insertion. The great reactivity of the Si—H bond in $HSiCl_3$ does not allow the resulting $:SiCl_2$ to be added to unsaturated compounds [40].

2.2. Synthesis on the Basis of Perchloropolysilanes

Application of hexachlorodisilane and higher perchloropolysilanes as a source of dichlorosilylene has appreciably expanded the synthetic potentiality of pyrolytic heterocyclization. A highly efficient generation of $:SiCl_2$, based on a one-step thermal decomposition of perchloropolysilanes (α-elimination reaction):

$$Cl_3Si\,(SiCl_2)_nSiCl_3 \xrightarrow{500\,^\circ C} SiCl_4 + (n+1):SiCl_2 \qquad (29)$$

$n \geqslant 0$

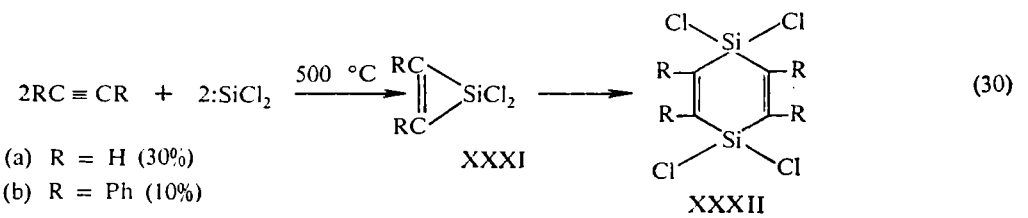
has made it possible to gain some insight into the behaviour of $:SiCl_2$ in gas-phase reactions as applied to synthesis of heterocycles. Here, chemical, kinetic, and spectroscopic evidence of formation of $:SiCl_2$ in thermal reactions was obtained for the first time [41-45]. The great reactivity of thermally generated dichlorosilylene and the appreciable selectivity of its interaction with certain chemical bonds have made it possible to synthesize the novel classes of het-

erocycles having one or two silicon atoms in the ring, whose production by other methods was difficult or impossible. To date the gas-phase reactions involving $:SiCl_2$ and underlying the numerous original techniques of preparing silicon-containing heterocyclic systems [16, 46-48] can be divided into three groups:

1. Addition to unsaturated C—C bonds.
2. Insertion into single C—H, O—H, or O—C bonds.
3. Detachment of the chlorine from some *o*-chlorine-substituted siliconaromatic compounds followed by intramolecular cyclization.

2.2.1. Addition of Dichlorosilylene to Unsaturated C—C *Bond*

Numerous examples have been used to describe addition of $:SiCl_2$ to an unsaturated bond in the gaseous phase. The yields of adducts are reasonably high and, in some instances, are quantitative. For instance, the reactions of $:SiCl_2$ with acetylene and tolan are of particular importance for a preparative synthesis of previously inaccessible tetrachloro-substituted 1,4-disilacyclo-2,5-hexadienes [24, 25, 40-42, 46]:



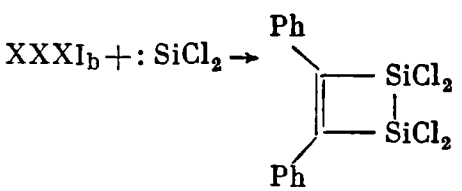
(a) R = H (30%)
(b) R = Ph (10%)

XXXI

XXXII

(30)

The reaction first step appears to involve addition of $:SiCl_2$ to an acetylene bond giving the corresponding derivative of silacyclopropene XXXI as an intermediate. Modest yields of XXXIIb arise from the formation of a new heterocyclic compound, 1,2-disilacyclo-3-butene, XXXIII, which can be thought of as a product of insertion of $:SiCl_2$ into the silacyclopropene ring:

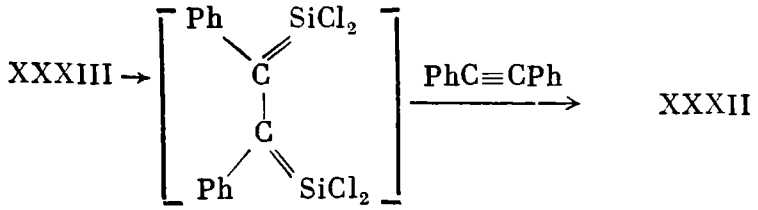


XXXIII (15%)

(31)

Formation of XXXII can be attributed either to σ-dimerization of silacyclopropene XXXI or to the Diels-Alder addition of diphenylacetylene to the intermediate 1,4-disila-1,3-butadiene resulting from the ring opening of XXXIII, as was expected for dimethyl- and

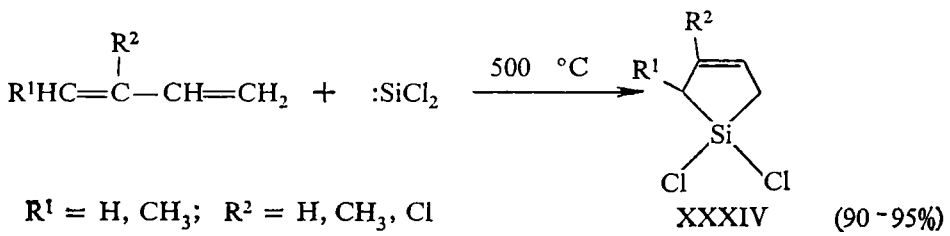
diphenylsilylenes [49]:



(32)

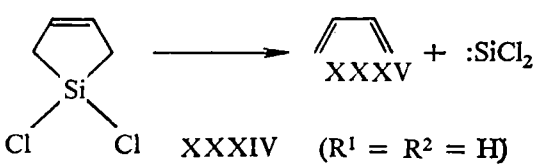
A close study of the reaction between diphenylacetylene and XXXIII in the range 500-600 °C has demonstrated the stability of the latter and, consequently, shown that under the given conditions the reaction cannot proceed along such a pathway. For this reason the assumption that the mechanism of σ-dimerization is primarily responsible for the formation of disilacyclohexadiene XXXII remains the most acceptable for the time being.

Thermal generation of $:SiCl_2$ from perchloropolysilanes has offered efficient ways to synthesize the simplest unsaturated organosilicon heterocycles in nearly quantitative yields on the basis of conjugated dienes, that is various derivatives of silacyclopentene [24, 25, 40, 42, 46]:



(33)

The reaction between hexachlorodisilane and 1,3-butadiene is first order for hexachlorodisilane and zero order for 1,3-butadiene [50]. The mechanism of this reaction remained unclear for a long time. The problem has been solved by a recent study into the thermal conversions of 1,1-dichloro-1-silacyclo-pentene-3 [51, 52]. At 500 °C the latter is unstable and generates dichlorosilylene according to the scheme of retrodiene decomposition [52]:

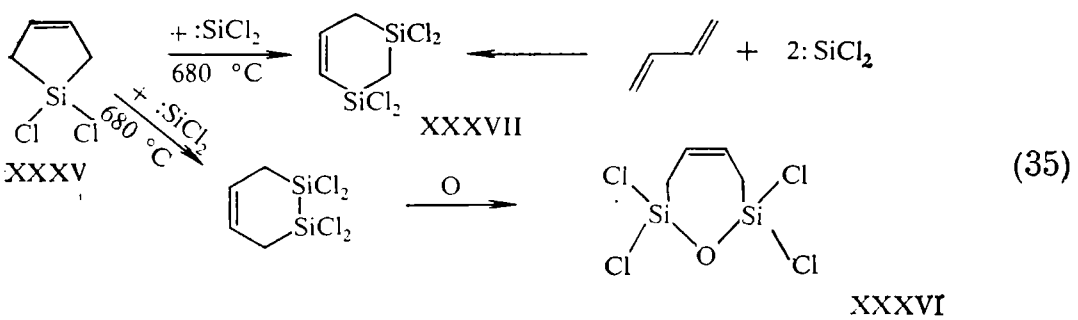


(34)

Chemical [52] and mass-spectroscopic [53] evidence indicates that the decomposition of XXXIV (R¹ = R² = H) is concerted and formally corresponds to the Diels-Alder retroreaction. This suggests that the gas-phase interaction of dichlorosilylene with *s-cis*-butadi-

enes-1,3 (scheme 34) corresponds formally to the Diels-Alder reaction and, consequently, unlike carbenes, follows the mechanism of concerted 1,4-cycloaddition. The ability of XXXIV ($R^1 = R^2 = H$) to generate $:SiCl_2$ has been used for a preparative high-temperature synthesis of new heterocyclic structures having two silicons in the ring, viz. 1,1,3,3-tetrachloro-1,3-disila-2-oxacycloheptene-5 (XXXVI) and 1,1,3,3-tetrachloro-1,3-disilacyclohexene-4 (XXXVII). On pyrolysis of XXXV (680 °C), the yields of XXXVI and XXXVII are 25 and 45%, respectively [51].

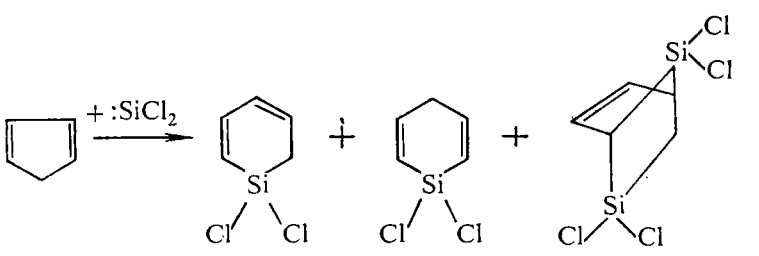
The mechanism of their formation can be explained only by an intermediate generation of $:SiCl_2$, which subsequently reacts either with the starting silacyclopentene or with 1,3-butadiene present in the reaction zone:



(35)

Combining with the Si—Si bond seems to be unstable and, on pyrolysis, it is converted into the end compound XXXVI. The yields of XXXVI and XXXVII decrease with decreasing temperature and at 500 °C they are 3 and 7%, respectively.

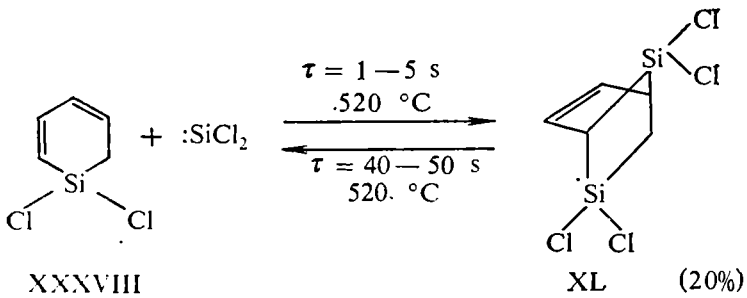
The reaction of dichlorosilylene with cyclic dienes, such as cyclopentadiene and furan, has produced several new silicon-functional heterocyclic systems [2, 24, 25, 40-42, 54]. For instance, the reaction between $:SiCl_2$ and cyclopentadiene results in heterocyclics XXXVIII-XL (the yields cited are optimal under the conditions of directed formation of each of them) [54].



(36)

Under the optimal conditions of formation of XXXVIII (520 °C, contact time 40 s), XL is prepared in modest yields which is the re-

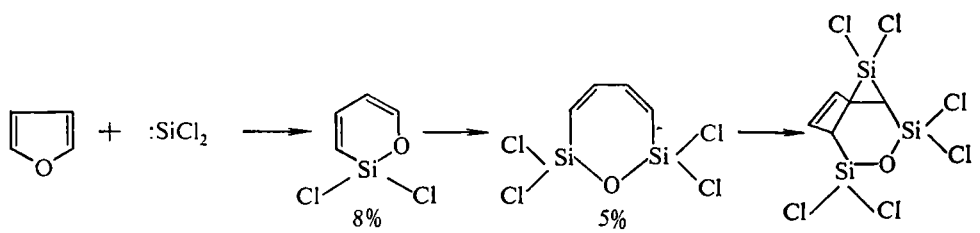
sult of its certain instability. The ratio of structural isomers XXXVIII and XXXIX does not practically vary with temperature. This can suggest that the reaction passes via the same intermediate stabilized by two different routes into XXXVIII and XXXIX. The previously unknown bicycle XL must be the product of 1,4-cycloaddition of $:SiCl_2$ to cyclic diene XXXVIII which is formed in the first step of the reaction [54]:



XXXVIII XL (20%) (37)

The reaction is reversible. Under conditions that are more severe than optimal ones, the resulting adduct, XL, is capable of dissociating into the starting components.

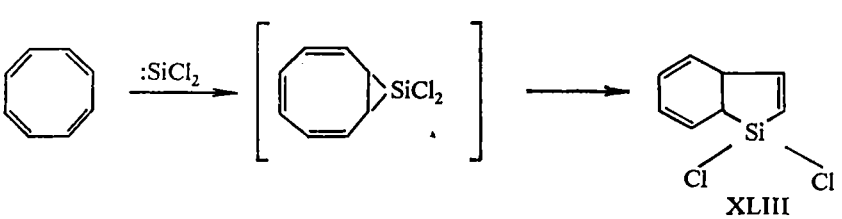
A bicyclic compound having three dichlorosilyl fragments, XLII, is, however, the main product of the gas-phase interaction of furan with dichlorosilylene generated from hexachlorodisilane [25, 40-42]:



XXIXa XLI XLII (38)

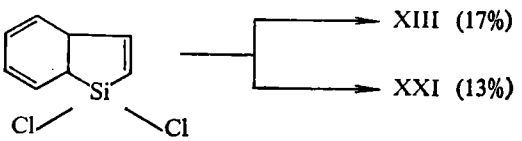
The scheme of reaction (38) has been borne out through experiments [25]. Cycloheptadiene XLI reacts with $:SiCl_2$ faster than does cyclohexadiene XXIX. This makes it difficult to prepare individual XLI.

The reaction between dichlorosilylene and cyclooctatetraene likewise generates heterocyclic compounds [2, 25, 55]. In this case, both the products of primary addition of $:SiCl_2$ and those of their further conversions are formed:



XLIII (39)

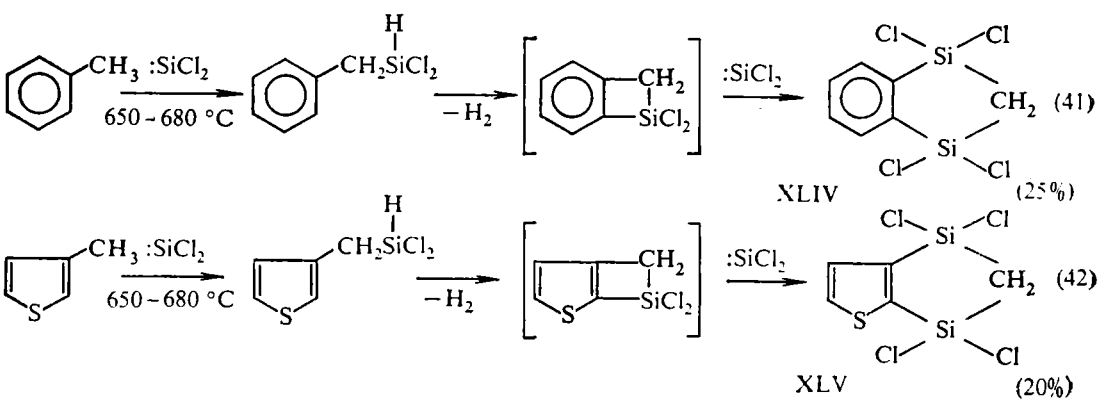
1,1-Dichloro-1-sila-8,9-dihydroindene (XLIII) is rather unstable at elevated temperatures and undergoes dehydration to form 1,1-dichloro-1-silaindene (XIII). Isomerization of XLIII also occurs in part to give 1,1-dichloro-1-silaindan (XXI):



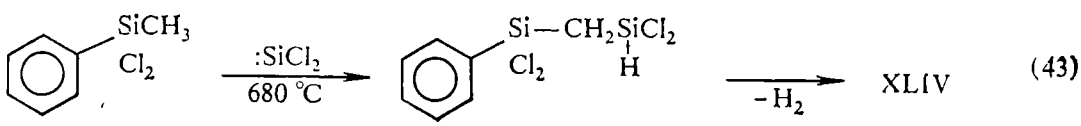
(40)

2.2.2. Insertion of Dichlorosilylene into C—H, O—H, or O—C Bonds

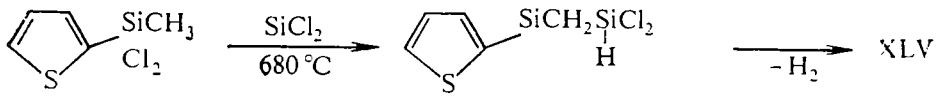
Gas-phase reactions involving insertion of $:SiCl_2$ into single bonds likewise give rise to heterocyclic systems [24, 25, 47, 56, 57]. The interaction of $:SiCl_2$ with C—H bonds has been investigated most extensively. A general mechanism by which such reactions occur has been elucidated: heterocyclic structures are formed due to conversions of the primary products of insertion through their intramolecular cyclization and a subsequent stabilization on insertion of the second molecule of $:SiCl_2$, e.g. [24, 25, 47, 56, 57]:



The same heterocyclic systems were prepared on insertion of $:SiCl_2$ into the C—H bonds of a methyl group at the silicon atom [24, 25, 56, 57]:

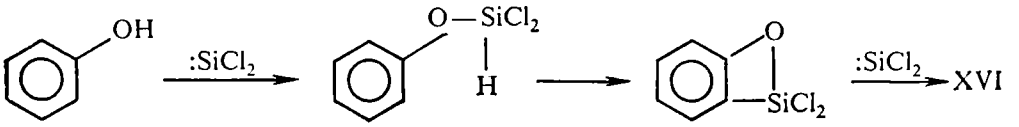


(43)



(44)

The gas-phase method has been successfully used to synthesize a new heterocyclic compound, 1,1,3,3-tetrachloro-2-oxa-1,3-disilaindan (XVI, R = Cl) [58]:



(45)

This reaction offers the first example illustrating formation of the insertion products of $:SiCl_2$ into the O—H and C—O bonds.

2.2.3. Cyclization with Detachment of Chlorine

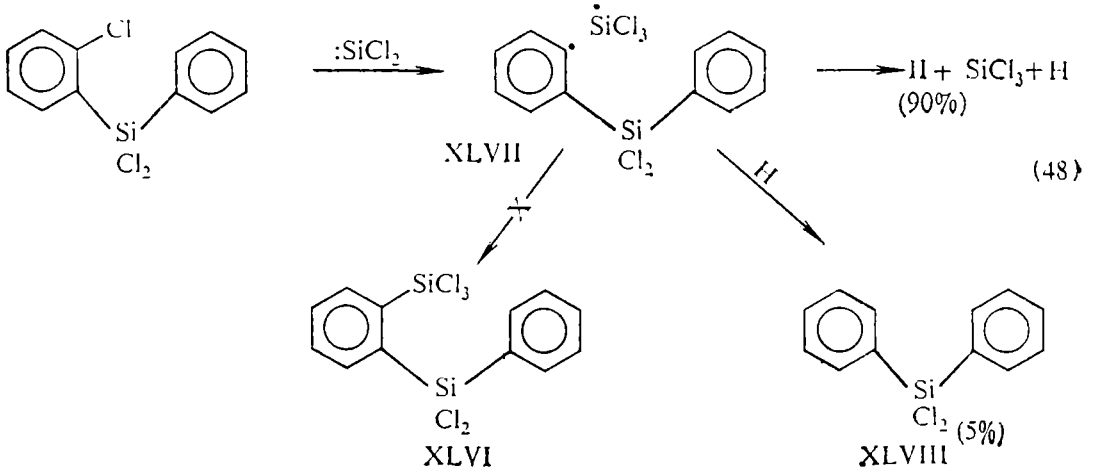
When hexachlorodisilane is used for the high-temperature syntheses of acyclic organosilicon compounds, insertion of $:SiCl_2$ into C_{ar}—Cl and C_{alk}—Cl exhibits high selectivity and appears to proceed through detachment-recombination steps. The same mechanism is followed when singlet carbenes interact with C—Cl bonds [59]. A singlet $:SiCl_2$ can also be assumed to detach the chlorine from the starting compound to afford a pair of radicals, whose recombination between each other gives the corresponding organyltrichlorosilane in high yield [60, 61]. The separation of the radical pair is not typical of this interaction, e.g.:

$$C_6H_5Cl + :SiCl_2 \xrightarrow{450-500\ ^\circ C} \underset{70\%}{C_6H_5SiCl_3} + \underset{\text{up to } 5\%}{C_6H_6} \quad (46)$$

$$ClCH_2SiCl_3 + :SiCl_2 \xrightarrow{580\ ^\circ C} \underset{55\%}{Cl_3SiCH_2SiCl_3} + \underset{\text{up to } 5\%}{CH_3SiCl_3} \quad (47)$$

A new gas-phase reaction of formation of silicon-containing heterocycles, which involves dichlorosilylene, has been detected. $:SiCl_2$ interacts thermally with some derivatives of *o*-chlorophenylsilane to detach nothing but the chlorine; however, while favouring intramolecular cyclization, it does not enter into the composition of the resulting heterocycle [16, 25, 48]. For example, the reaction between phenyl(*o*-chlorophenyl)dichlorosilane and hexachlorodisilane at

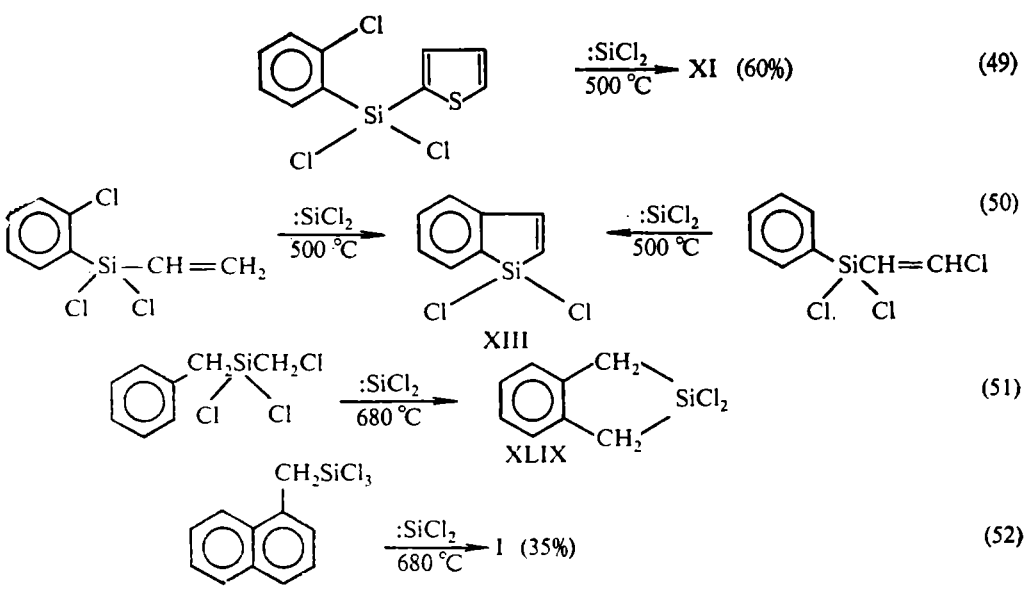
500 °C gives 9,9-dichloro-9-silafluorene (II) in 90% yield [25, 48]:



(48)

Although the reaction starts with a selective detachment of the chlorine by chlorosilylene, the product of its insertion into the C_{ar}—Cl bond, that is, into compound XLVI, due to the recombination of the radical pair, is not formed obviously on account of the pronounced tendency of a phenyldichlorosilyl radical XLVII for intramolecular cyclization. The formation of XLVIII as a result of the volume recovery of radical XLVII involving hydrogen elimination also fits into the proposed scheme.

The reaction between dichlorosilylene and organosilicon compounds containing a structural fragment capable of undergoing cyclization furnishes a foundation for a new generally applicable method of generating heterocyclic systems [16, 25]. This can be exemplified as follows:

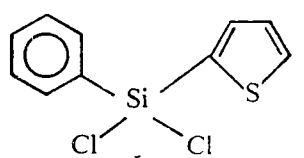


Cyclization of the aforementioned compounds under the same conditions but lacking a source of dichlorosilylene occurs to a small degree (below 7% yield), if at all. The lack of insertion products in reactions (49)-(53) indicates that after the chlorine has been detached by dichlorosilylene, cyclization is much more favourable than all other possible options of interaction.

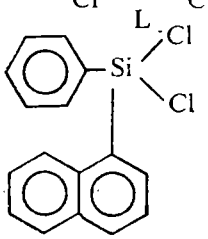
3. THERMAL CYCLIZATION OF ARYLCHLOROSILANES IN THE PRESENCE OF HALOGENATED ALKANES AND ALKENES

A novel cyclization reaction involving arylchlorosilanes in the presence of halogenated methanes, ethylenes, and hexachloroethane is also synthetically valuable [18, 25, 62-65]. For instance, at temperatures ranging from 550 to 680 °C, pyrolysis of diphenyldichlorosilane in the presence of halogenated methanes ($CHCl_3$, CH_2Cl_2, CH_2F_2, and CCl_4), ethylenes (di-, tri-, and tetraderivatives), and ethanes (C_2Cl_6) results in 9,9-dichloro-9-silafluorene (II) [25, 62, 63]. The yield of II in the presence of halogenated methanes amounts to 30-40% [25, 62]. Utilization of chlorinated ethylenes and hexachloroethane raises the yields of II to 55-60% [25, 63].

The other organosilicon heterocycles of the aromatic series have been prepared in a similar manner [18, 25, 62-65]:

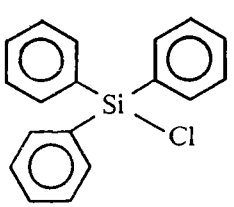


$\xrightarrow[600\ °C]{CHCl_3}$ XI (45%) (53)



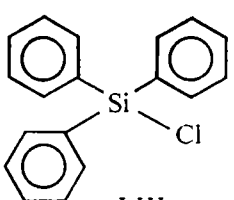
LI

$\xrightarrow[580\ °C]{CHCl=CCl_2}$ VII (20%) (54)

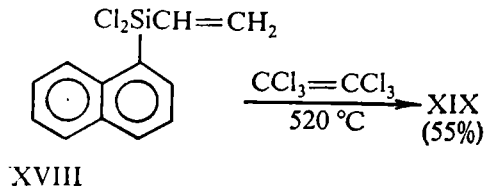


LII

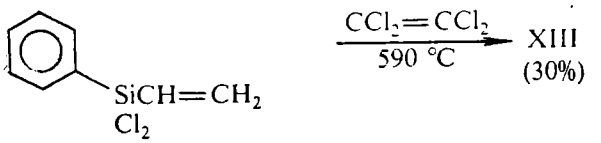
$\xrightarrow[570\ °C]{CCl_2=CCl_2}$



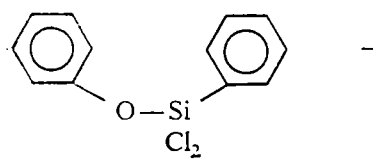
LIII (25%) (55)



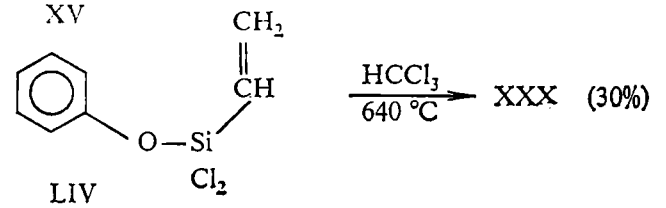
XVIII (56)



XX (57)

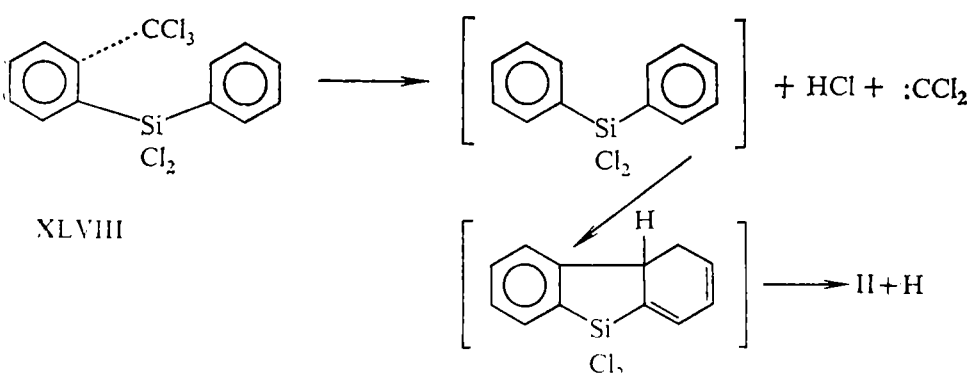


XV (58)



LIV (59)

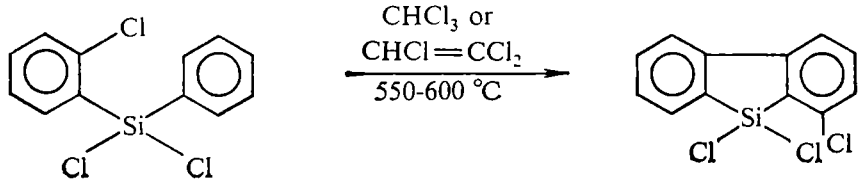
In the absence of the initiators referred to above, pyrolysis of compounds XV-XLVIII, L-LII, and LIV does not practically give rise to cyclization products. Intramolecular dehydrocyclization of XVIII and XX (cf. Section I) occurs even at higher temperatures (630-680 °C) in considerably smaller yields (20-25%). To date the mechanism of these reactions is not adequately understood. An appreciable contribution to the cyclization processes under discussion is most likely made by unstable intermediate particles, radicals and carbenes, whose formation suggests a thermal decomposition of the aforementioned halogenated hydrocarbons [59, 66, 67]. The role of the above intermediates seems to boil down to creating conditions for intramolecular homolytic arylation, that is, to an intermediate formation of a free radical having an unpaired electron at the *ortho*-carbon, as in cyclization of XLVIII:



XLVIII (60)

Since in the presence of such a source of a methyl radical as methyl iodide [68] cyclization does not occur, the expected reaction with chlorine-containing intermediates is presumably due to the tendency displayed by the reacting system to form a thermodynamically stable molecule of hydrogen chloride. As to free-radical aromatic substitution occurring in compounds where a radical centre and an aromatic system are spatially brought close together, examples are numerous [69].

The high selectivity of the involved heterocyclization process occurring solely via C_{ar}—H bonds has been demonstrated for the gas-phase interaction between *o*-chlorophenylphenyldichlorosilane and chloroform or trichloroethylene [25]:



(61)

Such reactions, where an intermediate compound merely favours cyclization without entering into composition of the resulting end products, have been reported in Section 2.1 with reference to dichlorosilylene, a silicon analogue of carbene. However, cyclization involving dichlorosilylene proceeds in a selective fashion provided the C_{ar}—Cl bond has been broken.

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7 Phenheterasilines and Their Analogues

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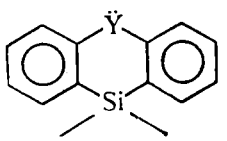
1. INTRODUCTION

Organosilicon compounds have outstanding technological and physiological properties that make them useful materials for furthering scientific and technological progress. These properties are due to the structural features of the silicon atom and its ability to interact in ways unlike carbon. For this reason, silicon compounds that exhibit specific electronic effects due to the silicon and, most importantly, can be observed, attract much attention. This category of compounds includes the comparatively little-studied but very unusual dihydroanthracene analogues in which the carbon atoms in the central ring are replaced by a silicon and a donor atom that has an unshared electron pair:



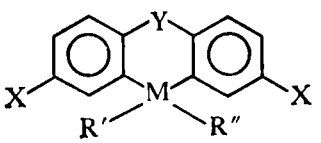
where $\ddot{Y} = \ddot{N}R$, $\ddot{O}$, $\ddot{S}$, etc.

These compounds were named phenheterasilines (phenaza-, phenoxa-, phenthia-, etc. silines). They are remarkable for their ability to interact with both the donor heteroatom and the acceptor heteroatom (silicon) having low vacant orbitals via the π electron systems of any (or both) of the equivalent phenylene groups. Since this interaction is symmetric and the number of electrons in the central phenheterasiline ring complies with Huckel's rule $(4n + 2)$, it can be expected that the central heterocycle will have an aromatic (or similar) character. These features seem to determine not only the specificity of the electron density distribution but also a number of the properties of phenheterasilines that have practical importance. For instance, the compounds of this class manifest the properties of antioxidants [1-3] and biological activity [4-8].

Thorough investigations into the structure and properties of phenheterasilines that compare them with those of their analogues which contain other group IV elements (germanium, tin) instead of silicon are undoubtedly useful. They help to develop the understanding of the nature of chemical bonds which are formed by non-transition elements and the rules governing their physiological and antioxidant activity [9, 10].

2. QUANTUM-CHEMICAL STUDY

The character of intramolecular effects in phenheterasilines and their analogues can be evaluated by quantum-chemical calculations. These calculations are possible only if information is provided on the valent state of the heteroatoms, the populations of the atomic orbitals, the coefficients of their hybridization, and the overlapping integrals of the orbitals of the heteroatoms and of the π electron systems of the phenylene groups. A series of calculations was made by the CNDO-2 method using the semiempirical Santry-Segal parameters as the *spd* basis for a number of derivatives containing silicon, germanium, and tin (I-IX):



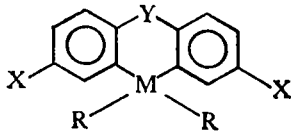
Compound	Y	M	R′=R″	X	Reference
I	NC_2H_5	Si	CH_3	H	[11]
II	O	Ge	Cl	H	[12]
III	O	Ge	CH_3	H	[13]
IV	S	Ge	C_6H_5	H	[12]
V	NC_2H_5	Ge	C_6H_5	H	[13]
VI	NC_2H_5	Ge	C_6H_5	Br	[13]
VII	NC_2H_5	Sn	C_6H_5	H	[13]
VIII	NC_2H_5	Sn	O—$CH_3C_6H_4$	H	[13]
IX	NC_2H_5	Sn	O—$CH_3C_6H_4$	Br	[13]

The results obtained by the calculations are listed in Tables 1 and 2. It is quite clear that the *d* orbitals contribute greatly to the hybrid orbitals of the atom of the group IVB element; their contribution decreases in the series Si > Ge > Sn. Also, the population of the $n_\pi Y$ orbitals diminishes in the series Si < Ge < Sn, and the $\langle \pi_1 M \mid \pi_2 M \rangle$ overlapping integrals of the atoms of the group IV element linking together the phenylene cycles follow the series Si > > Ge > Sn. The variation of the positive charge at the heteroatom (Si > Ge > Sn) and that of the negative charge (S < N < O) correlate completely with the effects evaluated. The unusual position of the sulphur in the last series is apparently caused by a strong contribution by the *d* orbitals to the hybrid orbital of the sulphur.

Thus, the data from the semiempirical calculations indicate that an atom of the element belonging to group V or VI (Y) and an atom

Table 1. Valent Configurations of Y and M Atoms

B



I Y = NEt, M = Si, R = CH_3
II Y = O, M = Ge, R = CH_3
III Y = S, M = Ge, R = Ph
IV Y = NEt, M = Ge, R = Ph
V Y = NEt, M = Sn, R = Me, X = Br
VI Y = O, M = Ge, R = Ph
VII Y = NEt, M = Sn, R = Tol
VIII Y = NEt, M = Sn, R = Tol, X = Br
IX Y = NEt, M = Ge, R = Ph, X = Br

Compound	Atom	Valent configuration	Charge q_M (Y)	References
I	Si	$3s^{0.9}3p^{1.8}3d^{1.2}$	+0.13	[11]
	N	$2s^{1.2}2p^{4.0}$	−0.19	[11]
II	Ge	$4s^{1.0}4p^{1.7}4d^{1.2}$	+0.11	[12]
	O	$2s^{1.6}2p^{4.6}$	−0.23	[12]
III	Ge	$4s^{1.0}4p^{1.8}4d^{1.1}$	+0.14	[12]
	S	$3s^{1.8}3p^{3.9}3d^{0.4}$	−0.18	[12]
IV	Ge	$4s^{1.0}4p^{1.9}4d^{0.9}$	+0.07	[13]
	N	$2s^{1.2}4p^{4.0}$	−0.19	[13]
V	Sn	$5s^{1.3}5p^{1.7}5d^{0.9}$	+0.07	[13]
	N	$2s^{1.25}2p^{3.95}$	−0.19	[13]

Table 2. Populations of the Hybrid Orbitals, $n_\pi Y$, and Overlapping Integrals, $\langle \pi_1 M | \pi_2 M \rangle$

Compound*	Atom	$n_\pi Y$	$\langle \pi_1 M \mid \pi_2 M \rangle$
I	N	1.83	—
	Si	—	0.58
IV	N	1.82	0.96
	Ge	—	0.41
V	N	1.89	0.70
	Sn	—	0.48
II	O	1.86	0.99
	Ge	—	0.30
III	S	1.95	0.34
	Ge	—	0.35
VI	O	1.87	0.97
	Ge	—	0.38
VII	N	1.88	0.72
	Sn	—	0.44
VIII	N	1.88	0.75
	Sn	—	0.45
IX	N	1.83	0.88
	Ge	—	0.47

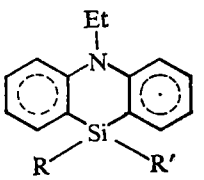
* For symbols see Table 1.

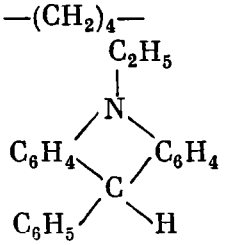
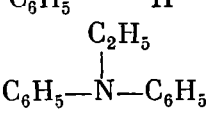
of the group IV element (M) interact with the π system of phenylene rings, and hence interact with the Y—C_6H_4—M fragment previously discussed. The sensitivity of the parameters being considered to the effect of the substituent in the phenylene rings (Br) also demonstrates that this interaction occurs. These calculations are of limited importance unless there is experimental evidence of the connection between the structure and physical and chemical properties; however in combination with data of this sort, the calculations become reliable.

3. SPECTRAL STUDIES

The specific features of the structure and intramolecular interactions of phenheterasilines and their analogues can be determined by analysis of the absorption and emission spectra in different regions, from ultraviolet to radio-frequency.

Table 3. UV Spectra of Phenazasilines and Their Analogues



R	R′	λ_{max} (log ε)
p-BrC_4H_6	H	285 (4.09), 305 (3.86), 330 (3.76)
p-ClC_4H_6	H	285 (4.01), 305 (4.1), 330 (3.75)
C_6H_5	H	285 (4.24), 305 (4.15), 330 (3.86)
p-$CH_3C_4H_6$	H	285 (4.24), 305 (4.11), 330 (3.83)
p-$CH_3OC_4H_6$	H	285 (4.19), 306 (4.09), 330 (3.80)
n-C_4H_9	H	287.5 (4.20), 300 (4.22), 325 (3.71)
cyclo-C_6H_{11}	H	287.5 (4.24), 325 (3.84)
CH_3	CH_3	287.5 (4.24), 320 (3.72)
—$(CH_2)_4$—		290.0 (4.01), 300 (3.88), 330 (3.53)
		292.5 (4.27)
		297.0 (4.18)

Electronic spectra can ascertain the effect of the broadening of the conjugation system and should therefore be considered first. The UV spectra of phenazasilines (I-III) and of dihydroacridine (IV) and diphenylamine (V) with similar structures show (Table 3) that

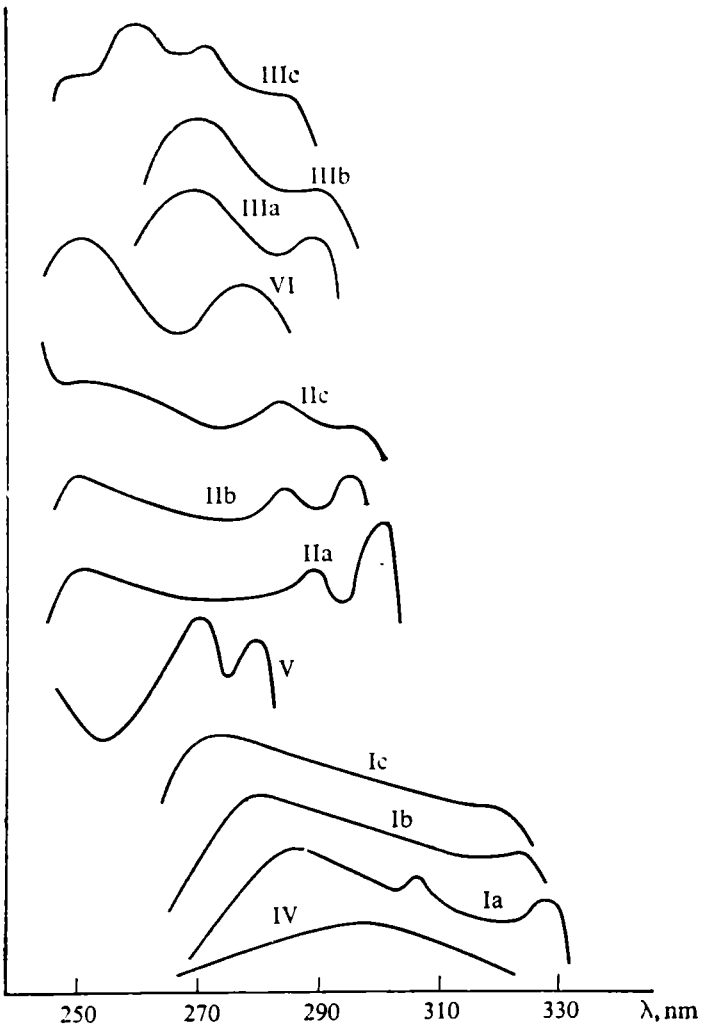
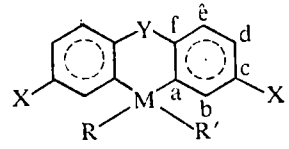


Figure 1. UV spectra of phenheterasilines, -germines, -stannines, and their analogues with the unclosed cycle

the closure of the middle ring shifts the long-wave maximum 297.5 nm towards shorter wavelengths and that the substitution of the carbon atom in the heterocycle by silicon causes new permitted levels in the long wavelength region (305 and 330 nm) [14]. These new long-wave maxima are very sensitive to the structure of the heterocycle. Their shift depends on the nature of heteroatoms M and Y, of the substituents linked to them, and of the substituents in the benzene ring (Fig. 1). All this indicates that these molecules have a new

Table 4. IR and ^{13}C NMR Spectroscopic Data for  Compounds

M	R	R′	X	Y = N–C$_2$H$_5$		Y = S		Y = O	
				ν_{C-Ar}, cm^{-1}	$\delta C_{M,Y}$, ppm	ν_{C-Ar}, cm^{-1}	$\delta C_{M,Y}$, ppm	ν_{C-Ar}, cm^{-1}	$\delta C_{M,Y}$, ppm
Si	C_6H_5	C_6H_5	H	1585	122.5, 150.3	1573	132.7, 143.8	1592	133.9, 160.0
Ge	C_6H_5	C_6H_5	H	1578	125.2, 150.3	1568	133.9, 144.9	1578	135.2, 160.0
Sn	C_6H_5	C_6H_5	H	1569	127.2, 153.6	1566	—	1570	—
Si	C_6H_5	C_6H_5	Br	1570	—	1580	—	1592	—
Ge	C_6H_5	C_6H_5	Br	1565	—	—	—	—	—
Si	C_6H_5	CH_3	H	1570	—	—	—	—	—
Si	CH_3	CH_3	H	—	—	1570	139.9, 134.1	1488	—
Ge	CH_3	CH_3	H	1580	—	—	139.4, 140.0	—	—
Sn	CH_3	CH_3	H	—	—	—	142.4, 145.6	—	—
Si	CH_3	CH_3	Br	1578	—	—	—	—	—
Si	CH_3	H	H	1590	—	1580	—	1590	—
Ge	CH_3	H	H	1582	—	1575	—	1590	—

conjugation system which is due to the delocalization of the electron density of the unshared electron pair of atom Y towards atom M with vacant orbitals. The degree of delocalization which can be identified with the degree of aromaticity, varies in the series N > O > S and Si > Ge > Sn. This basically agrees with the predictions [15]. The evaluation of the conjugation effect that was suggested on the basis of UV spectra analysis was supported by the results of IR and NMR studies. Absorption in the 1580 cm^{-1} region appears in the RI spectra of aromatic compounds only when the benzene ring is conjugated with an unsaturated group or with a heteroatom having an unshared electron pair [16]. The degree of conjugation affects the intensity of the absorption band and has a comparatively slight influence on its location. The data in Table 4 are consistent with these ideas: growth in the degree of delocalization of the unshared pair of heteroatom Y decreases the polarity of the C—Y bond and the stretching vibration frequency in the N > O > S series. A similar dependence is observed in the Si, Ge, Sn series. These phenomena are also evidenced by non-planar bending vibrations of the C—H bonds in the phenylene groups and by stretching vibrations of the C—M bonds observed in the long-wave IR region (200-500 cm^{-1}). Here these dependences are expressed very distinctly (frequency difference reaches 100 cm^{-1} and more) [17].

Very important information is provided by ^{1}H [15] and ^{13}C [18] NMR spectra. This technique was used to study the degree of shielding of the carbon nuclei that is directly linked to heteroatoms M and Y (C_M and C_Y). An analysis of the values for the chemical shifts given in Table 4 leads to a degree of conjugation series similar to those mentioned above, viz. Si > Ge > Sn and N > O > S. The presence of an electron acceptor substituent (Br) in positions 2 and 8 shifts the C_M signals downfield (to a lesser extent for C_Y). This relates to a decrease in the total degree of conjugation of the system.

All these data refer to the ground state of molecules of phenheterasilines (—germines, —stannines), and need further corroboration from studies of the molecules in states other than the ground state (excited or intermediate). To the latter group belong charge transfer states. Information on states different from the ground state should be useful in evaluating the reactivity of phenheterasilines and their analogues.

4. STUDY OF CHARGE TRANSFER COMPLEXES AND EXCITED STATES

The ability of phenheterasilines and their analogues to conjugate was evaluated. Quantitative characteristics of the conjugation were obtained on the basis of electron spectra of charge transfer complexes of these compounds with such acceptors as tetracya-

noethylene [19] and oxygen [20]. An example of benzene and its derivatives was used to show that the dependence of the charge transfer frequencies on the structure of the molecule permits evaluation of the degree of conjugation in the system [21]. Table 5 lists charge transfer frequency values for the series of phenheterasilines and their derivatives. The following conclusions can be drawn from these data:

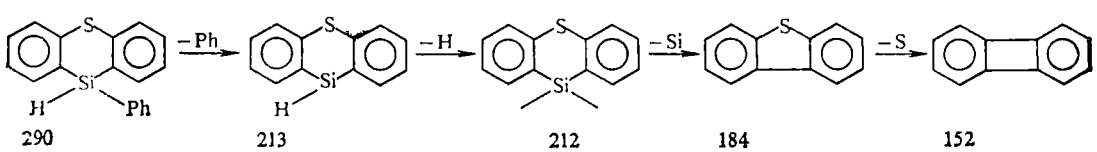
(a) the character of the effect of substituents in the phenylene groups is similar to that observed for benzene derivatives (compare compounds 1-3 and 4-6);

(b) the degree of participation of the electron pair of heteroatom Y in conjugation decreases in the series N > S > O (compare compounds 1, 15, 29 and 2, 16, 30);

(c) when Y is unchanged, the degree of conjugation follows series Si > Ge > Sn in accordance with the relative ability of IVB group elements to interact with the participation of vacant orbitals.

Since the charge transfer state lies between the ground and electron-excited states, the frequencies of the O, O transition, ν_e, which were determined by the joint analysis of the electron absorption and emission spectra, were taken for the evaluation of conjugation in the latter state (Table 5). It can be seen that for the excited state, a decrease in the aromatic character of the heterocycles in the series N > S > O is similar to that found for the charge transfer state. A linear correlation is observed between ν_e and ν_{ct} ($\nu_e = 0.58$, $\nu_{ct} = +\ 21\ 400$, $r = 0.996$ [1]) which can also indicate that these compounds conjugate [22]. More detailed information about the character of charge transfer complexes is provided by the emission spectra for complexes of phenheterasilines and their analogues with molecular oxygen [20]. In silicon derivatives, the largest contribution belongs to the interaction of oxygen with the π electron system of the aromatic rings, whereas when M = Sn, the local interactions (πv type) between oxygen and tin prevail. These properties correspond to the greater ability of the silicon atom to form conjugated systems. The general principles found for oxygen charge transfer complexes (CTC) are analogous with those discussed for CTC with tetracyanoethylene.

The excited state of the molecules can be characterized by studying their stability and fragmentation during an electron impact. Thus, 10-phenylphenthiasiline decomposes in the following way [3]:



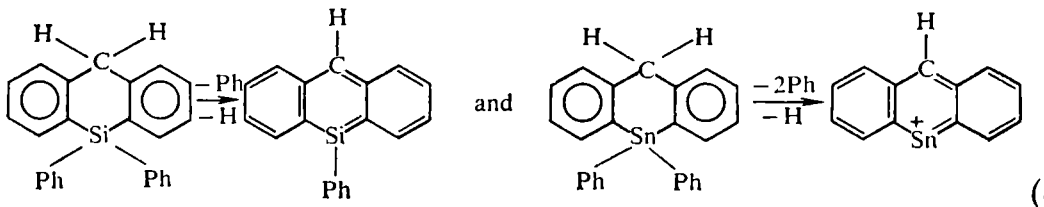
290 213 212 184 152

From this it can be seen that the phenyl radical linked to the silicon is split off easier than the hydrogen. This phenomenon can be ex-

Table 5. Frequencies of Charge Transfer, ν_{ct}, and O, O Transition, ν_e

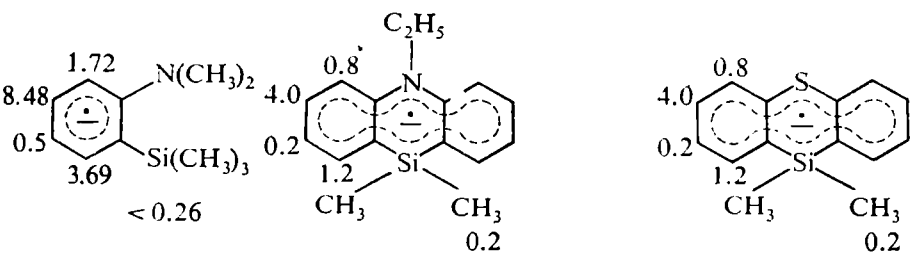
M	R	R′	X	No.	Y = NC_2H_5		No.	Y = S		No.	Y = O	
					$\nu_{ct} \cdot 10^{-3}$, cm^{-1}	$\nu_e \cdot 10^{-3}$, cm^{-1}		$\nu_{ct} \cdot 10^{-3}$, cm^{-1}	$\nu_e \cdot 10^{-3}$, cm^{-1}		$\nu_{ct} \cdot 10^{-3}$, cm^{-1}	$\nu_e \cdot 10^{-3}$, cm^{-1}
Si	C_6H_5	C_6H_5	H	1	11.9	28.4	15	16.1	30.5	29	17.9	30.0
Ge	C_6H_5	C_6H_5	H	2	12.1	29.0	16	16.4	31.5	30	17.9	32.6
Sn	C_6H_5	C_6H_5	H	3	13.7	29.0	17	16.8	32.6	31	18.0	32.8
Si	C_6H_5	C_6H_5	Br	4	13.8	—	18	—	—	32	—	—
Ge	C_6H_5	C_6H_5	Br	5	14.0	—	19	—	—	33	—	—
Sn	C_6H_5	C_6H_5	Br	6	14.3	—	20	—	—	34	—	—
Si	C_6H_5	C_6H_5	H	7	12.8	28.8	21	17.5	31.2	35	17.9	31.8
Si	CH_3	CH_3	H	8	11.1	—	22	—	—	36	—	—
Ge	CH_3	CH_3	H	9	12.1	29.4	23	—	—	37	17.8	32.5
Sn	CH_3	CH_3	H	10	—	—	24	—	—	38	—	—
Si	C_6H_5	H	H	11	11.3	—	25	—	—	39	—	—
Si	CH_3	CH_3	Br	12	13.1	—	26	—	—	40	—	—
Si	CH_3	H	H	13	—	—	27	—	—	41	—	—
Ge	CH_3	H	H	14	—	—	28	—	—	42	—	—

plained by the participation of the silicon in the overall conjugation system of the heterocycle, hence hampering its conjugation with the phenyl radical undergoing detachment. It is worth noting that the decomposition scheme is similar to the schemes found for sila- and stannanedihydroanthracenes that involves formation of an ion with an aromatic system [23, 24]:



(3)

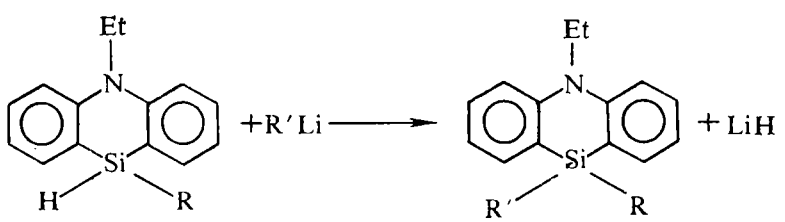
The ESR spectra of anion radicals formed when phenaza- and phenthiasilines react with metallic potassium [25] provide a direct proof that conjugated systems can form by the participation of two heteroatoms—donor and acceptor. The hyperfine structure splitting constants of the unpaired electron with aromatic protons in the anion radicals are about half as large as the constants in the 2-trimethylsilyl-N,N-dimethylaniline anion radical [26]:



This fact can be explained by spin density delocalization in the anion radicals of phenheterasilines.

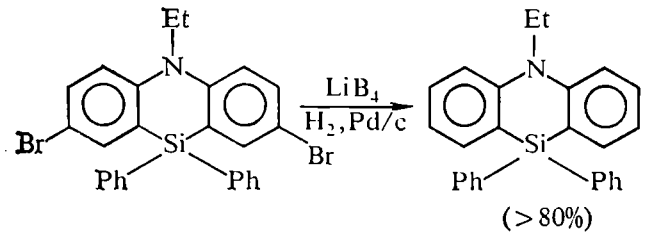
5. REACTIVITY

Phenheterasilines and their analogues can react in ways that preserve the heterocycle; some reactions are typical aromatic compound reactions. For instance, phenazasilines containing an Si—H bond react with organolithium compounds to give the corresponding aryl- or alkyl-substituted products in a yield that approaches 80% [27]:



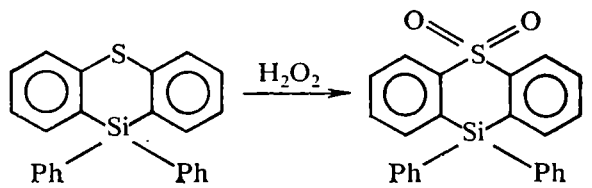
(4)

The action of butyllithium or hydration in the presence of Pd/C substitutes hydrogen for bromine in 2,8-dibromo-5-ethyl-10,10-diphenylphenazasiline [26]:



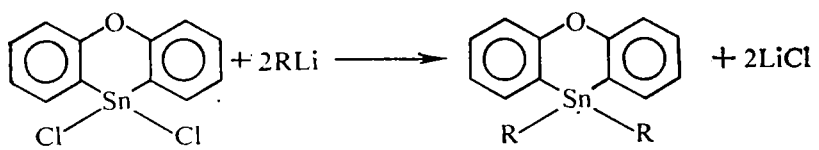
(5)

10,10-Diphenylphenthiasiline is easily oxidized by 30% hydrogen peroxide to form the corresponding sulphone [29]:



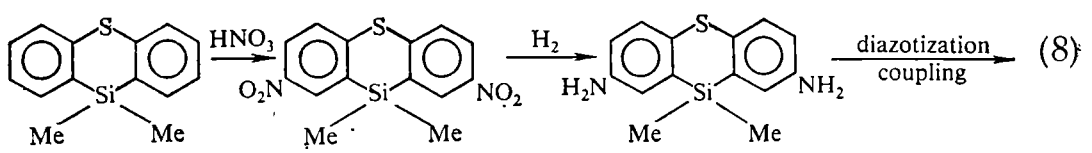
(6)

10,10-Dichlorophenoxastannine, by interacting with organolithium or -magnesium compounds, yields the corresponding Sn-substituted derivatives [30]:



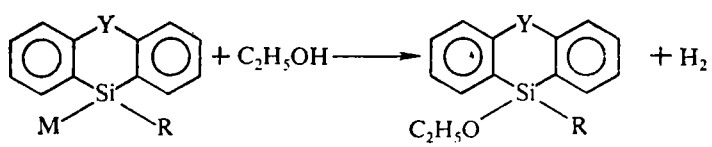
(7)

Nitration of phenthiasilines followed by reduction and dye synthesis conforms to this scheme [31]:



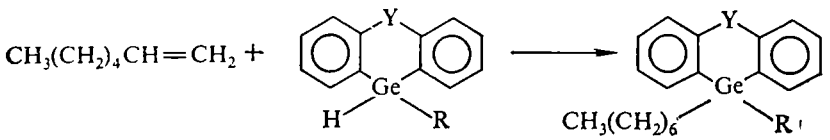
(8)

Systematic studies of the reactivity of phenheterasilines and -germines were performed on an example of compounds containing the M—H bonds. The kinetics of the reactions of phenheterasilines with ethanol in the presence of a base (sodium alcoholate) was studied [3]:



(9)

The rate of the reactions of phenheterasilines decreases, depending on heteroatom Y, in the O > S > N sequence. The same series is applicable to 1-heptene hydrogermylation by phenheteragermines containing the Ge—H bond [10]:



(10)

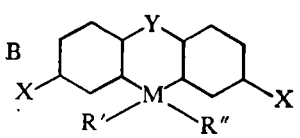
The dependences obtained by kinetic measurements and physical methods indicate that there is a conformity between the hydride reactivity series and the degree of the participation of heteroatoms in the conjugation system of molecules in the excited state (N > S > > O). The conformity is related to the increase in the degree of conjugation in heteroatoms Y and M which decreases the electrophility of the latter and hence the reactivity of the compound.

It follows from this that the reactivity of phenheterasilines and their analogues should be evaluated on the basis of studies of excited molecules which are carried out by physical methods.

6. STRUCTURE STUDIES. GEOMETRY AND PROPERTIES

The spatial structure of phenheterasilines and their analogues determines their properties as well as the differences in the properties of molecules in the ground and excited state. Most phen-

Table 6. Values of the Dihedral Angles, ω, in



Compounds

M	Y	R′	R″	X	ω, °	References
Si	NC_2H_5	C_6H_5	C_6H_5	H	157.3	[32]
Si	NC_2H_5	C_6H_5	C_6H_5	Br	138.8	[33]
Si	NC_2H_5	CH_3	CH_3	Br	140.9	[34]
Si	$N(CH_2)_2C_6H_{10}N$	CH_3	CH_3	H	143.0, 147.4	[35]
Si	S	CH_3	CH_3	H	148.0	[36]
Si	S	CH_3	CH_2Cl	H	141.3	[36]
Si	SO_2	CH_3	CH_3	H	134.1, 143.0	[37]
Ge	O	Cl	Cl	H	180.5	[38]
Ge	S	CH_3	CH_3	H	143.6	[39]

heterasilines and their analogues are essentially non-planar, the central heterocycle having the boat shape and the dihedral angle between the phenylene fragments differing from 180° (Table 6). It follows from the table and Figs. 2 to 4 that there is a certain correlation between the structure and properties of phenheterasilines and their analogues. For instance, the value of the dihedral angle depends on

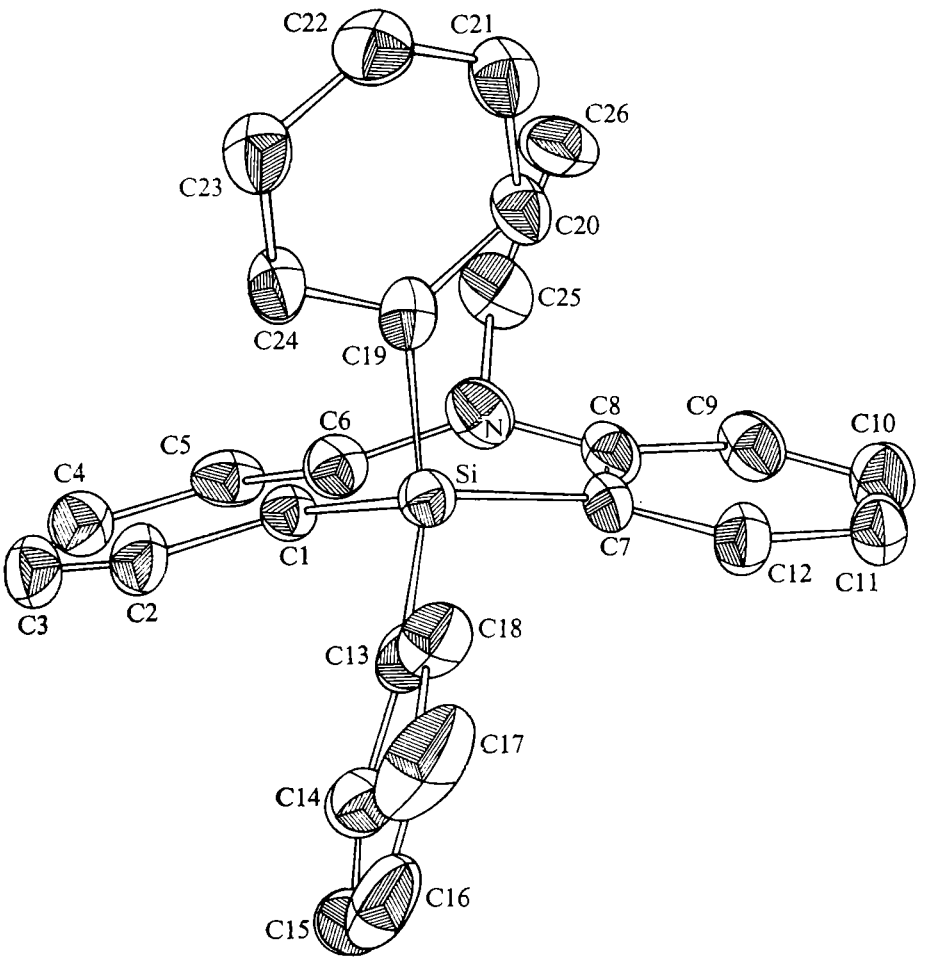


Figure 2 5-Ethyl-10,10-diphenylphenazasilin.

the nature of heteroatom M, and on the substituents at M and in the phenylene groups. This dependence led to the assumption that the degree of conjugation in the heterocycle should be the larger as the molecule conformation becomes more planar. In individual cases this assumption was supported by experimental data. In general, however, this opinion proved to be incorrect. For example, 10,10-dimethylphenoxasiline is almost planar when the dihedral angle between the planes of the phenylene fragments is 175.5° [40]. This value is much larger than it could have been expected on the basis of the results of physical and chemical studies of the dependence of the

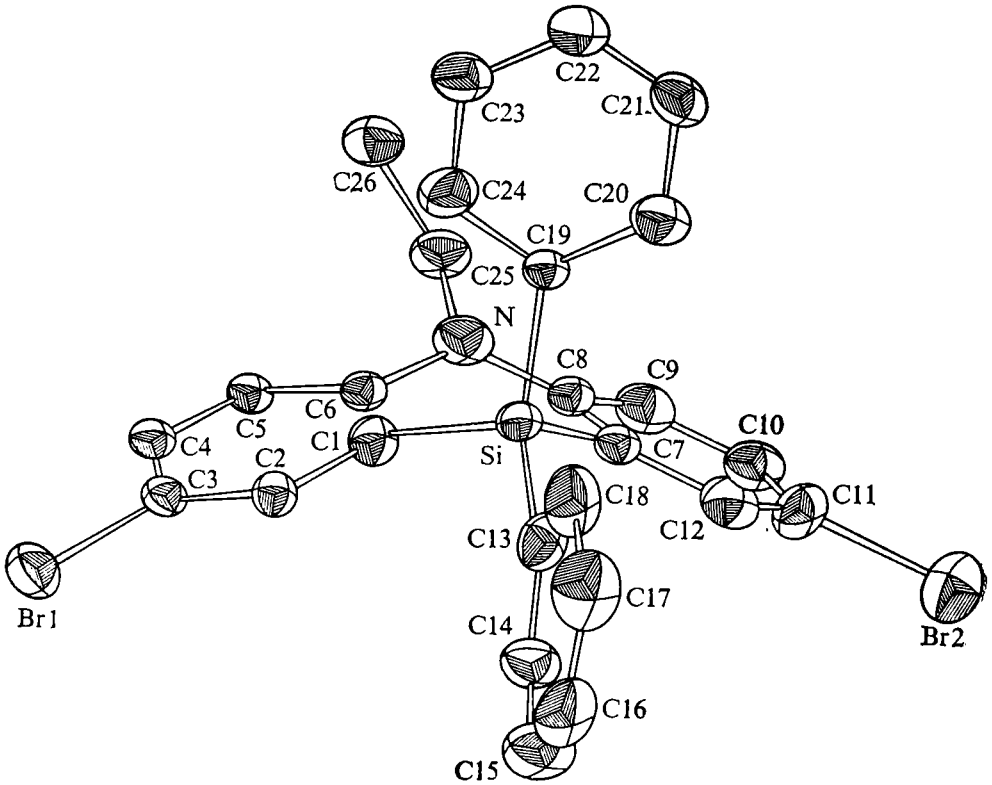


Figure 3. 2,8-Dibromo-5-ethyl-10,10-diphenylphenazasiline

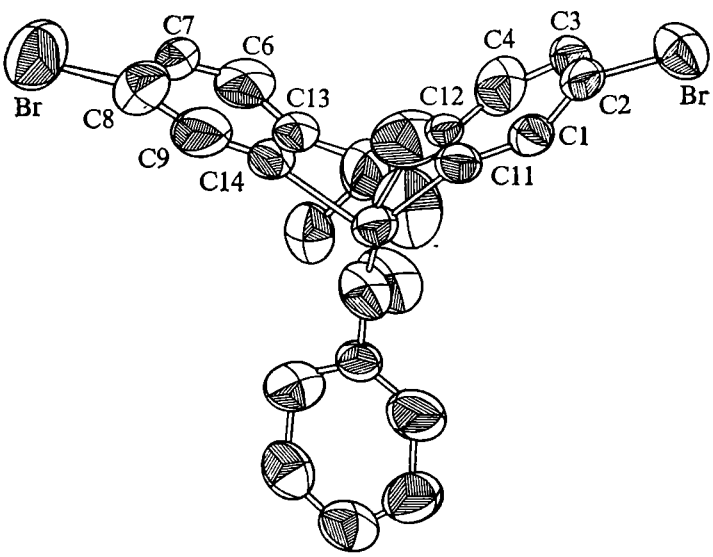
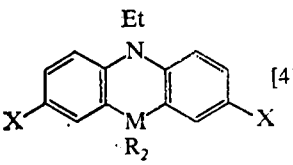


Figure 4. 2,8-Dibromo-5-ethyl-10,10-diphenylphenazastannine

degree of conjugation on the nature of heteroatom Y (N > O > S and N > S > O). Unfortunately, no data on the conformation of the central heterocycle are available. Nevertheless, the arguments against the dependence of the properties on the size of the diherdal angle [40] should be taken into consideration. It follows from Table 6 that in phenheteragermines at Y = O the dihedral angle is greatly enlarged. Systematic studies on the conformation of phenheterasilines and their germanium- and tin-containing analogues [41] (Tables

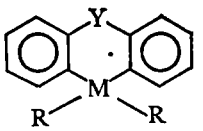
Table 7. Structure Parameters of the  [41]

Compounds

M	R	X	Dihedral angle, °	C–M–C angle, °	C–Y–C angle, °	M–C *endo*, Å	M–C *exo*, Å	N–C *endo*, Å	N–C *exo*, Å
Si*	Me	Br	140.9	98.7	120.0	1.855	—	1.425	—
Si*	Ph	H	157.3	101.1	124.5	1.849	—	1.406	—
Si	Ph	Me	141.4	100.4	121.8	1.849	1.867	1.415	1.471
Si*	Ph	Br	138.8	99.8	121.3	1.857	—	1.394	—
Si	*o*-Tol, OMe	Br	161.5	100.4	125.2	1.834	1.868	1.413	1.474
Ge	Ph	H	156.1	99.9	124.9	1.922	1.940	1.410	1.471
Ge	Ph	Br	138.2	98.1	122.0	1.927	1.939	1.416	1.478
Ge	Ph, Cl	Me	146.6	100.1	121.8	1.920	1.939	1.429	1.474
Sn	Ph	Br	125.2	92.0	118.0	2.124	2.142	1.440	1.470
Sn	*o*-Tol	H	129.6	93.4	118.2	2.126	2.140	1.434	1.479
Sn	*o*-Tol	Me	124.4	93.0	116.9	2.127	2.142	1.436	1.472
Sn	*o*-Tol	Br	133.3	92.6	119.2	2.132	2.140	1.439	1.473

* Literature data (Table 6).

7 and 8) together with the preceding data all show that the endocyclic C—M—C angles are much smaller than the tetrahedral angle. Heteroatom M is located far from the plane in which the carbon atoms of the heterocycle are arranged [41]. On the whole, all the molecules studied are non-planar and bended along the M ...Y axis. The size of the dihedral angle grows in the series Sn < Ge < Si and depends on the nature of Y (O > N > S), of the substituents at atom M (aryl < alkyl), and of the substituents in the 2, 8 positions (H > > Me > Br). Thus, the variation in the conformation of the molecules correlates with changes in their characteristics as conjugated sys-

Table 8. Structure Parameters of the  [41]

Compounds

M	Y	R	Dihedral angle, °	C–M–C angle, °	C–Y–C angle, °	M–C *endo*, Å	M–C *exo*, Å	Y–C *endo*, Å
Si	O	C_6H_5	165.9	101.2	125.2	1.852	1.866	1.386
Si**	O	CH_3	175.5	100.4	125.5	1.850	—	1.375
Ge	O	C_6H_5	165.8	99.1	126.4	1.928	1.939	1.388
Ge*	O	Cl	170.5	105.4	127.0	1.900	—	1.370
Si*	S	CH_3	148.0	104.6	107.1	1.862	—	1.767
Si	S	C_6H_5	150.4	105.9	107.2	1.858	1.870	1.774
Ge*	S	CH_3	143.6	102.7	106.3	1.934	—	1.773

* Literature data (Table 6).
** [40].

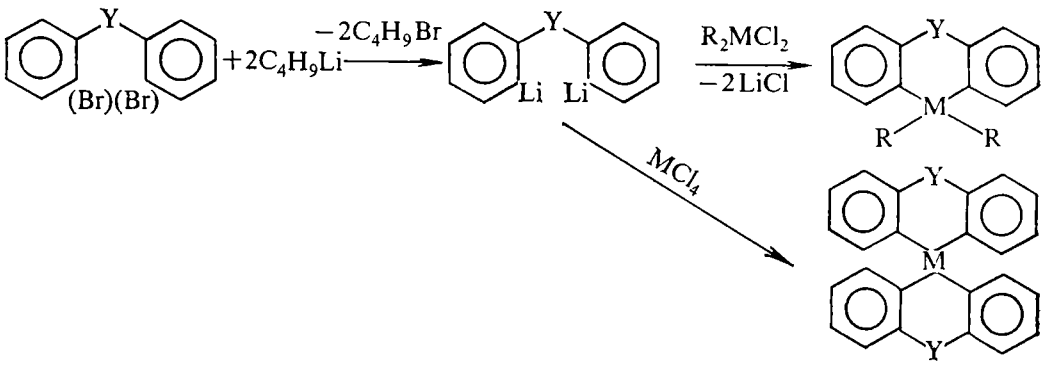
tems. The correlations are observed only within narrow groups of compounds. No generalized dependence can be established. However, the conjugation effect is undoubtedly reflected in the geometric parameters of the molecules. This statement is also supported by the noticeable shortening of the M—C *endo* bonds as compared with the *exo* bonds. They are particularly strong in the case of phenheterasilines, being between 0.01 and 0.04 Å (measurement error 0.003-0.006 Å). The drastic reduction of the length of the C—N *endo* bond as against the *exo* bond (0.03-0.06 Å) also supports this statement.

These data suggest that the conjugation effects take place in phenheterasilines and their analogues regardless of their non-planar configuration. When applied to purely organic molecules, this conclusion seems to be incorrect since non-planarity hampers the overlapping of the electron clouds of the π bonds. However, with phenheterasilines and their analogues, non-planarity is not an obstacle to effective overlapping because conjugation involves the participation not only of *p* but also of *d* orbitals which have large diffuseness and a different angular electron density distribution.

7. METHODS OF SYNTHESIS

Phenheterasilines and their analogues can be obtained in several ways: organometallic synthesis, dehydrocyclization of diphenyl derivatives, and heteroatom exchange reaction.

The general scheme of organometallic synthesis first proposed by H. Gilman [27] has (apart from the preliminary stages) two stages: lithiation of $(C_6H_5)_2Y$ or $(2\text{-}BrC_6H_4)_2Y$ and the interaction of synthesized 2,2′-dilithium substituted compounds with halogen derivatives of the corresponding elements of the IVB group. The synthesis of the 2,2′-dilithium derivative of diphenylamine proceeds from 2,2′-dibromo derivative [27]; dilithium derivarives of diphenyloxide and diphenylsulphoxide are obtained by direct lithiation with butyllithium [30]:

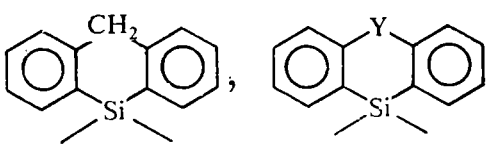


(11)

where Y = NC_2H_5, X = Br; Y = O, SO_2, X = H; M = Si, Ge, Sn.

The initial $(2\text{-}BrC_6H_4)_2S$ required for the synthesis of phenthiasilines is obtained via 2-bromo-2′-aminodiphenyl sulphide which undergoes diazotization followed by substitution of bromine for the diazo group with the help of excess Cu_2Br_2 [42].

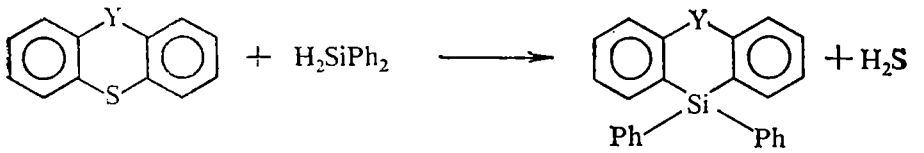
The high-temperature condensation of aromatic compounds with chlorosilanes gave rise to silicon-containing heterocycles whose structure is very similar to that of phenheterasilines [43]:



This method proved to be useful in preparing 10,10-dichlorophenoxagermine [38]. It is evident that regardless of its low selectivity, the high-temperature condensation method is a promising possibility for the commercial synthesis of phenheterasilines and their analogues. This is due to its simplicity, single-stage character, and the availability of the initial reactants.

A comparatively simple (at first glance) method of preparing phenheterasilines (following the Yur'ev reaction type) was employed by

H. Gilman as early as in 1957 [44]:



(12)

where Y = O, S, SO_2, NH, NEt.

The process runs at 260-270 °C at a very low rate (3 days) and gives insignificant yields (2-4%). For this reason the prospects of a future practical use of this method are dubious.

8. CONCLUSION

Phenheterasilines and their analogues containing a heteroatom of germanium or tin are distinguished by a number of specific features. The most important of these is the transfer of electron density from the donor atom (Y = O, S, N) to the atom of the IVB group element (M = Si, Ge, Sn) via the π system of phenylene rings. Because of this, the central heterocycle and hence the whole of the tricyclic system are characterized by behaviour resembling aromatic. The planar structure of the molecules is not obligatory for this interaction to occur. This particular fact is a serious experimental corroboration that vacant (probably, *d*) orbitals of the IVB group atom do participate when interacting with electron-donor systems. Earlier this was indicated only by indirect evidence. It can be thought that the specific features of the electron structure of phenheterasilines and their analogues are responsible for their peculiar properties, including biological activity. In this sense they resemble silatranes and their analogues in which intramolecular (true, transannular) interaction which involves the participation of vacant orbitals of the heteroatom of silicon also takes place.

Unfortunately, the chemistry of phenheterasilines and their analogues has been insufficiently developed until now and the methods of their synthesis are complicated. Hopefully, further studies in this interesting domain of organoelement chemistry will bring results that will be important for both the theory and practice.

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8 Organosilicon Derivatives of Furan and Thiophene

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1. INTRODUCTION

Studies of furan and thiophene derivatives of silicon were started at the Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, 25 years ago. By now, a host of data on the synthesis, chemical, physicochemical, and biological properties of these compounds has been obtained. In this paper the results of our investigations of silicon-containing derivatives of furan and thiophene are generalized and systematized.

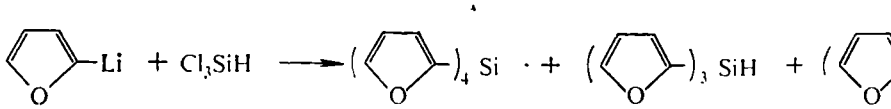
2. SYNTHESIS OF FURYL- AND THIENYLSILANES

A common method for the synthesis of furyl- and thienylsilanes is reacting 2- and 3-furyllithium [1-15], 2- and 3-thienyllithium [4, 15, 16] or 2-thienylmagnesium bromide [4, 15-20] with chloro- [1-20] or ethoxysilanes [4, 15, 16, 18] in an inert solvent:

(1)

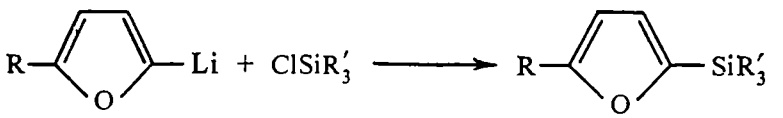
X = O, S; M = Li, MgBr; n = 1 - 4; Z = Cl, EtO

This method is also applicable to the synthesis, not only of alkylsilyl derivatives, but of compounds that in addition to a heterocyclic substituent at the silicon have a hydrogen atom [1-3, 6, 10, 17, 18, 21-23], a vinyl [4, 24], chloromethyl [4, 24, 21, 25] or ethoxy group [4, 15, 26, 27]. In some instances reaction (1) is accompanied by side processes. Thus, as a rule, the Si—H bond in hydrochlorosilanes is, during their interaction with organolithium compounds, substituted by an organic radical [1-4, 6, 16, 23, 28, 29]. The main product of the reaction of 2-furyllithium with trichlorosilane is tetra(2-furyl)silane. Tri- and di(2-furyl)silanes are also formed [21, 22, 29]:



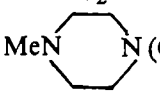
(2)

Organolithium synthesis can be also used for obtaining furan derivatives with a substituent in position 5 of the furan ring:



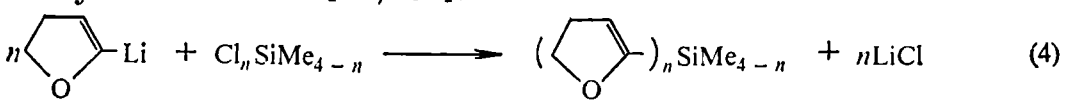
(3)

R = Me [1, 2, 5, 6], $(EtO)_2CH$ [30], Me_3Si [3, 5, 31, 32],

Me_3Ge [3, 31, 32],  [21, 22]

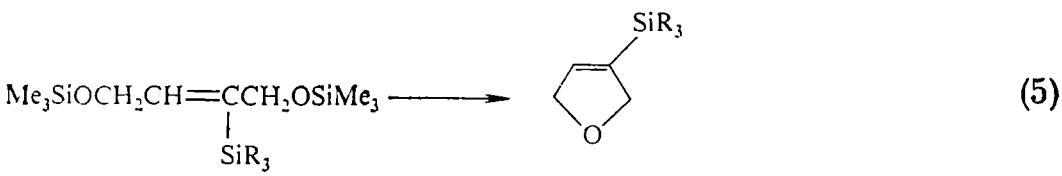
Furyl- and thienylmercurchlorides do not react with halosilanes [33].

A series of methyl[2-(4,5-dihydrofuryl)]silanes were obtained by interaction of the lithium derivative of 2,3-dihydrofuran with methylchlorosilanes [34, 35]:



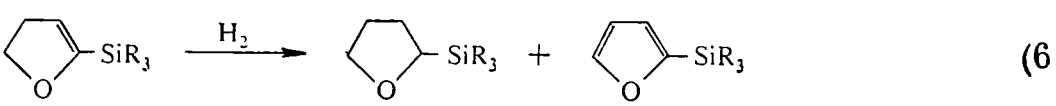
(4)

Organolithium synthesis of trimethylsilyl derivatives of 2,5-dihydrofuran failed because the 2,5-dihydrofuran cycle opened when butyllithium or lithium diisopropylamide was added [36]. The cyclization of bistrimethylsilyl ether of 2-trimethylsilyl substituted 1,4-butenediol was used to this end [36]



(5)

Catalytic hydrogenation of trialkyl[3-(2,5-dihydrofuryl)]- and trialkyl[2-(4,5-dihydrofuryl)]silanes on Pd/C, Pd/Al_2O_3, or in the presence of complex catalysts based on transition metals, such as Ru(II), Rh(I), Pd(0), Pd(II), gives trialkyltetrahydrofurylsilanes. Dehydrogenation and disproportionation that yield trialkylfurylsilanes run parallel with this reaction [37]:



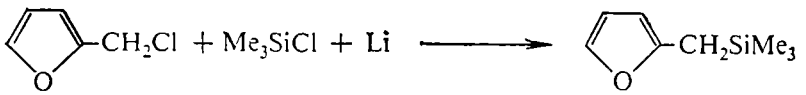
(6)

(7)

The yield of trialkylfurylsilane grows in non-polar solvents and at elevated temperatures [37].

Si-Substituted furfurylsilane in which silicon is separated from

the furan ring by a methylene group was obtained by reacting furfuryl chloride with trimethylchlorosilane and lithium [3, 8] or 2-furyllithium with chloromethyltriorganylsilanes [1-3, 8, 10, 14]:



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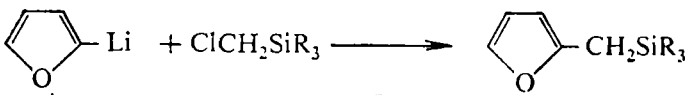
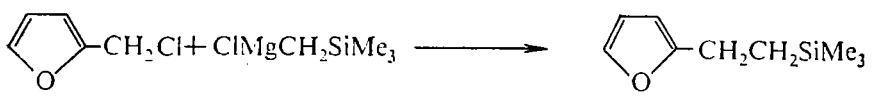


(9)

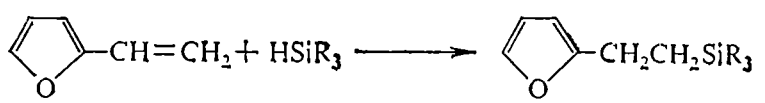
R = Et [2, 5], R = EtO [4, 5]

In the reaction between chloromethyltriethoxysilane and 2-furyllithium the Si—O bond participates in forming a mixture of substitution products [4, 15, 27]. Compounds with two methylene groups between the furan heterocycle and the silicon were synthesized from furfuryl chloride and trimethylsilylmethylmagnesium chloride [1, 2, 5]:



(10)

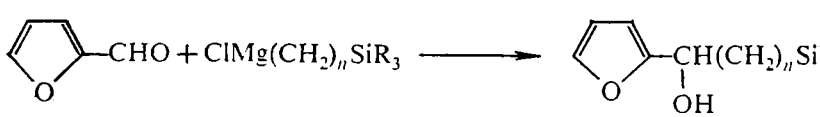
or by hydrosilylation of vinylfuran [1, 2, 38, 39] which in THF and dioxane proceeds in most cases with the formation of β adducts:



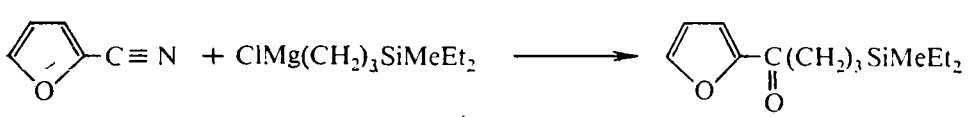
(11)

R = Et, Cl, EtO

Organosilicon derivatives of furan that contain a functional substituent in the methylene group linked to the heterocycle can be conveniently prepared by reacting silicon-containing organomagnesium compounds and furfural [1, 2, 5] or 2-cyanofuran [1, 2]:



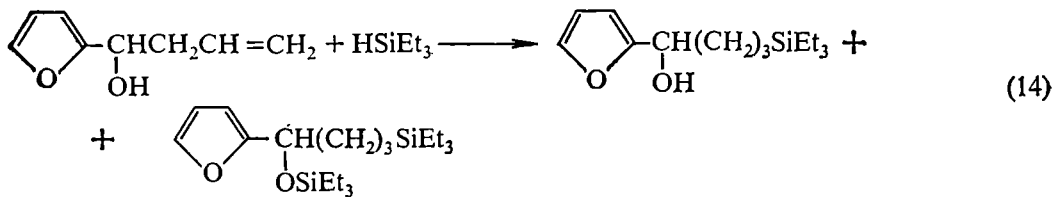
(12)



(13)

Hydrosilylation of 1-(2-furyl) but-3-ene-1-ol with triethylsilane in the presence of H_2PtCl_6 [1, 2, 40] gives a mixture of two adducts

with the silicon at the δ position with respect to the heterocycle:

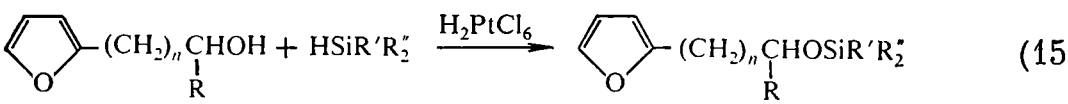


(14)

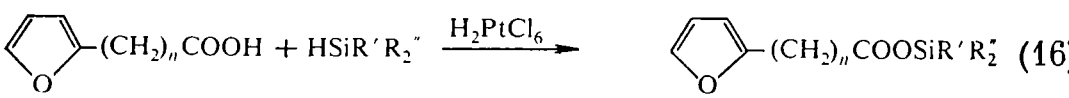
Organosilicon derivatives of furan in which the silicon is linked to a heteroatom (O, S, N) in the side chain were obtained by reacting corresponding alcohols [2, 41, 42-44], sodium mercaptides [2, 40], amines [2, 40], aldehydes [2, 45], oximes [2, 40], carboxylic acids [2, 46] and their amides belonging to the furan series with various silylating agents (trialkylchlorosilanes, trialkylsilanes, hexamethyldisilazane).

2-Furfurylamine [2, 40], furfural oxime [2, 40], and furfuryl alcohol [2, 42-44] react with methyl chlorosilanes in benzene, xylene or ether in the presence of a hydrogen chloride acceptor (pyridine, triethylamine, 2-furfurylamine in excess). 2-Furfurylmercaptane reacts slowly and in a low yield with dimethyldichlorosilane in the presence of pyridine. Reacting trimethylchlorosilane and sodium mercaptide gives slightly better results [2, 40].

Dehydrocondensation of trialkylsilanes with furan compounds containing a mobile hydrogen usually proceeds in the presence of chloroplatinic acid [2, 41-44]:



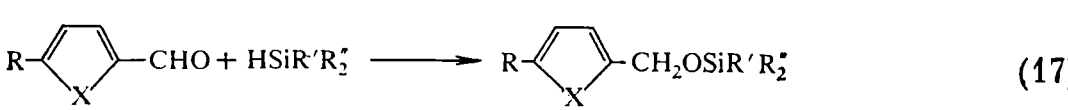
(15)



(16)

The reaction of dehydrocondensation with oximes is complicated by side processes that involve reduction and N—O bond splitting; this reduces the yield of *o*-trialkylsilyloximes to 34% [2, 40]. In the presence of H_2PtCl_6 2-furfurylamine does not react with triethylsilane when heated in THF or without solvent. However, in the presence of potassium furfurylamide the yield of triethyl(2-furfurylamino)silane is 77.5% [2, 40]. 2-Furfurylmercaptane does not react with triethylsilane under the action of H_2PtCl_6 [2, 40].

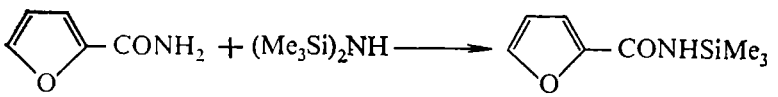
Trialkylsilanes slowly react with furfural and 2-thiophene aldehyde [2, 45] in the presense of Speier's catalyst during prolonged heating:



(17)

Under these conditions, triethylsilane is added to 2-acetylfuran with great difficulty [2, 45]; after 96 h of heating, the yield of the adduct is only 2.2%.

Pyromucic amide reacts easily with hexamethyldisilazane when heated to give a trimethylsilyl derivative in 92% yield [2, 40]:



(18)

3. PHYSICOCHEMICAL PROPERTIES

3.1. NMR Spectra

The general character of the NMR spectra of furan and thiophene derivatives is determined by the donor-acceptor influence of their substituents; for this reason the NMR technique was employed to investigate the electron effect of substituents with respect to the π electron system of the heterocylce in R_nSiMe_{4-n} compounds when R was 2-furyl [1-4, 12, 16, 31, 47-50], 3-furyl [12], 2-(4,5-dihydrofuryl) [24, 35], and 2-thienyl [4, 16, 18, 51, 52] (Table 1).

Chemical shifts by protons in the heterocycle observed in the spectra of 2 and 3-substituted methylfurylsilanes are displaced downfield in relation to corresponding carbon-containing analogues [3, 11, 12, 50]. All signals of the protons in the ring of 2-thienylmethylsilanes are also shifted downfield with respect to unsubstituted thiophene [3, 16]. In the PMR spectrum of trimethyl[2-(4,5-dihydrofuryl)]silane, δH (3) of the heterocycle features a 0.23 ppm downfield shift relative to the unsubstituted 2,3-dihydrofuran. Conversely, the methyl group in 2-methyl-4,5-dihydrofuran shifts the H(3) signal towards stronger fields. These data can be explained by the fact that the methylsilyl group has a strong acceptor influence on the π electron system of the heterocycle. An increase in the number of heterocyclic substituents at the silicon is accompanied by weaker shielding of the ring protons and methyl groups in all the series of compounds studied [3, 4, 11, 12, 16, 34, 50].

The ^{13}C NMR data indicate that trimethylsilyl and *tert*-butyl groups have the opposite effect on shielding of the furan ring. The organosilicon substituent $(CH_3)_3Si$— shifts the $\delta^{13}C$ values for all nuclei of the heterocycle downfield with respect to unsubstituted furan; the $(CH_3)_3C$ group shields C(3) and C(5) in 2-substituted furan and all nuclei of the ring in 3-substituted furan, except for C(3) to which it is directly linked [3, 12, 49]. The removal of the trimethylsilyl group from the furan ring by one or two methylene groups results in the loss of its acceptor capacity [3, 49, 50, 53].

Table 1. Chemical Shifts of ^{1}H, ^{13}C, ^{29}Si in the NMR Spectra of R_nSiMe_{4-n}

R	n	δ²⁹Si, ppm	δ¹H, ppm					δ¹³C, ppm				
			H(2)	H(3)	H(4)	H(5)	CH_3	C(2)	C(3)	C(4)	C(5)	CH_3
2-furyl	1	—11.5	—	7.56	6.27	6.52	0.26	160.2	120.0	109.7	146.7	—1.3
2-furyl	2	—24.7	—	7.59	6.29	6.64	0.51	157.1	121.8	109.9	147.4	—3.0
2-furyl	3	—39.2	—	7.61	6.30	6.77	0.80	154.3	123.8	110.2	148.2	—4.6
2-furyl	4	—56.0	—	7.67	6.36	6.89	—	151.4	125.5	110.4	149.1	—
3-furyl	1	—9.7	7.38	—	6.41	7.52	0.24	147.7	119.1	113.6	143.5	—0.3
3-furyl	2	—19.6	7.39	—	6.41	7.52	0.44	148.7	117.4	113.8	143.8	—1.1
3-furyl	3	—29.5	7.42	—	6.45	7.54	0.64	149.7	116.0	114.1	144.0	—1.6
3-furyl	4	—	7.44	—	6.49	7.57	—	150.5	114.3	114.3	144.3	—
2-(4,5-dihydrofuryl)	1	—11.0	—	5.20	2.59	4.28	0.16	162.7	110.8	31.1	70.6	—1.8
2-(4,5-dihydrofuryl)	2	—23.2	—	5.35	2.61	4.32	0.30	159.6	113.3	31.2	70.9	—3.9
2-(4,5-dihydrofuryl)	3	—37.1	—	5.53	2.65	4.35	0.45	156.4	115.6	31.3	71.1	—6.0
2-(4,5-dihydrofuryl)	4	—51.9	—	5.71	2.66	4.38	—	153.8	118.0	31.3	71.3	—
2-thienyl	1	—6.0	—	7.27	7.17	7.61	0.34	139.9	134.1	128.2	130.5	0.5
2-thienyl	2	—15.03	—	7.33	7.20	7.62	0.68	137.4	135.5	128.4	131.5	0.5
2-thienyl	3	—24.14	—	7.42	7.23	7.70	0.96	135.3	137.2	128.5	132.4	0.8
2-thienyl	4	—34.07	—	7.53	7.26	7.76	—	134.0	138.4	129.3	134.0	—

Substituting of a methyl group in tetramethylsilane by 2-furyl [3, 49], 3-furyl [12], 2-(4,5-dihydrofuryl) [34], 2-thienyl [4, 16] groups causes the silicon signals to shift upfield. The degree of silicon shielding increases linearly with the number of heterocyclic substituents in the molecule. Electron interaction between the silicon atoms and the π electrons of the ring decreases in the following order: 2-furyl > 2-(4,5-dihydrofuryl) > 3-furyl > 2-thienyl > phenyl.

According to NMR spectral data, silicon-containing substituents at the aromatic heterocycle in furyl- and thienylalkoxysilanes act as electron acceptors with respect to the π electron system; this effect decreases in the compounds in the following order: $Si(OEt)_3 >$ $> EtOSi(OCH_2CH_2)_2NMe > \underset{\downarrow}{Si}(OCH_2CH_2)_3\underset{|}{N}$. This is because of the growing competitive interaction between the silicon and the functional groups [4, 53]. As n increases in the $R_nSi(OEt)_{4-n}$ series (R = 2-furyl, n = 0-4), the signals of the H(4), H(5) protons, as well as the ring carbons move downfield; the dependence of the chemical shifts of silicon on n has a parabolic character with a minimum at $n = 3$. Adding one furyl radical to tetraethoxysilane shifts $\delta^{29}Si$ downfield by 14.4 ppm. This indicates that the π electron system of furan contribute less to silicon shielding than the ethoxy group [4, 53].

PMR studies have established that the chemical shifts of protons in furylsilanes depend on concentration. The nature of the solvent (CCl_4, dioxane, triethylamine, chloroform, cyclohexane, benzene) strongly affects the chemical shift of furan ring protons in methylfurylsilane (to 0.5 ppm) [54, 55]. Furylhydrosilanes feature weak intermolecular associations [54, 55].

3.2. Vibrational Spectra

The IR absorption spectra of the following compounds were studied: alkyl(2-furyl)silanes [1-3, 56-60], 2-furylhydrosilanes [1-3, 56], β-(2-furyl)ethylsilanes [1-3, 57], furfuryloxysilanes [2, 56], furfurylaminosilanes [2, 56], organosilicon esters and amides of pyromucic acid [2, 56], 2,5-disubstituted organosilicon derivatives of furan [2, 3, 31, 56], furylalkoxy- and furylaminoalkoxysilanes [61], and also Raman spectra of 2-furylsilanes [2, 56, 60] and β-(2-furyl)ethylsilanes [2, 56]. Then the algorithms of logical interpretation of IR spectra were elaborated, and the problems in assigning frequencies to the furan ring and organosilicon substituents were solved [62].

The stretching vibrations of the C—H bonds of furylsilanes have maxima at 3158 ± 5 cm^{-1} and 3127 ± 9 cm^{-1} in the IR spectra. The spectra of 2,5-disubstituted organosilicon derivatives of furan have a single band at 3110 ± 5 cm^{-1}. As the number of furyl groups

at the silicon atom grows, the intensity of the absorption band of the C—H bond increases [2, 3, 31, 56]. Vibrations with frequencies at 1610-1558, 1512-1470, 1405-1377, and 1010 ± 10 cm^{-1} were assigned to the skeletal vibrations of the ring. All the organosilicon derivatives of furan that we studied are characterized by a vibration at 605 ± 5 cm^{-1} (bending vibration of the furan ring). This IR band and the band at 1006 ± 6 cm^{-1} (pulsation vibration of the furan ring) indicate that the furan ring is present in the molecule [1, 3].

All organosilicon derivatives of furan have broad and intense absorption bands at 400-550 cm^{-1} assigned to the stretching vibrations of the $Si—C_{furyl}$ fragment. Increasing the number of furyl groups in methylfurylsilanes from one to four broadens the bands of this vibration, increases their intensity, and shifts them towards shorter waves [1, 56, 57].

3.3. UV Spectra of Charge Transfer Complexes

In order to evaluate the distribution of the electron density in the molecules of furyl- and thienylsilanes in the excited state, we studied their charge transfer complexes (CTC) using UV spectroscopy [1, 3, 4, 63-70]. The bands of CTC of trimethylsilyl derivatives of furan and thiophene with tetracyanoethylene are located in a region of larger frequencies [63-65] than those of corresponding carbon-containing compounds. These findings confirm a strong electron-acceptor effect of the trimethylsilyl group (Table 2).

Table 2. Frequencies for the Charge Transfer Bands (ν_{CT}, cm^{-1}) in the CTC Spectra of Furan and Thiophene Derivatives, R_nSiMe_{4-n}

R	Carbon analogue, $RCMe_3$	$n = 1$	$n = 2$	$n = 3$	$n = 4$
2-furyl	19150	20400	20900	22000	22750
3-furyl	20400	21200	21400	21700	21800
2-thienyl	19800	20450	20900	21140	21400

The accumulation of heterocyclic substituents at the silicon atom systematically raises ν_{CT}. However, the range of changes for 3-furyl and 2-thienyl derivatives is narrower than for 2-furylsilanes [64, 65]. The dependence between the frequencies of 2- and 3-furylsilanes in the CTC spectra is linear [64]:

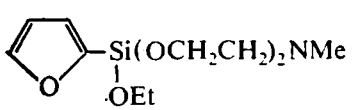
$$\nu^3_{CT} = 0.386\nu^2_{CT} + 13300 \quad (r = 0.999) \qquad (19)$$

Substituents, such as the chloromethyl group, exhoxy group, hydrogen atom, and the silatrane fragment, affect the charge transfer frequencies in the 2-furan and 2-thiophene series in a like manner [4, 65].

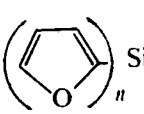
3.4. Chromatographic Properties

1-(2′-Furyl)- and 1-(2′-thienyl)silatranes have a sufficiently high vapour pressure that enables their chromatographic separation on polar and non-polar stationary phases when applied to "silanated" Chromosorb.

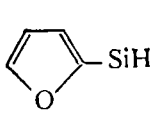
The retention indices on polar and non-polar stationary phases, ΔI, for furyl- and thienylsilatranes differ as much as 1300 [4, 71-73]. This greatly exceeds ΔI values for such chromatographic polarity standards as butanol, nitropropane, and pyridine. An additive calculation of the retention indices of silatranes containing 2-furyl and 2-thienyl groups based on the corresponding values for the structure fragments of their molecules are 200-1000 units lower than those obtained by experiment [71, 72]. The difference between the experimental and calculated values for the retention indices (δI) is determined both by the presence of a silatrane fragment with the transannular N → Si bond and by the nature of the substituent at the silicon atom. Regardless of a large molecular weight, 2-(2-furyl)-2-ethoxy-6-methyl-1,3-dioxa-6-aza-2-silacyclooctane,



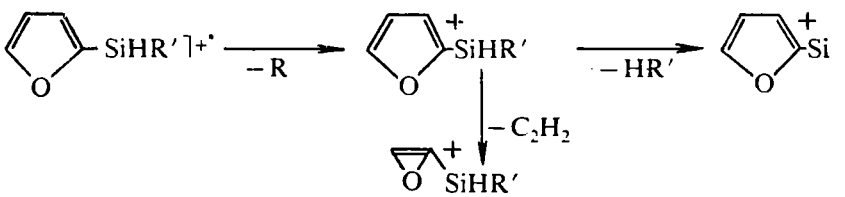
is eluted 9.6 times faster and 1-[β-(2-furyl)ethyl]silatrane 4.4 times faster than 1-(2-furyl)-silatrane [4, 73].

I and ΔI of methyl(2-furyl)silanes  increase drastically with an increase in the number of furyl groups (n) in the molecule [3, 9]. It seems that this phenomenon is due to the growth of the contribution of induction and orientation forces to the overall chromatographic retention effect.

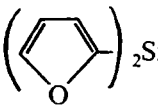
3.5. Mass-spectrometric Studies

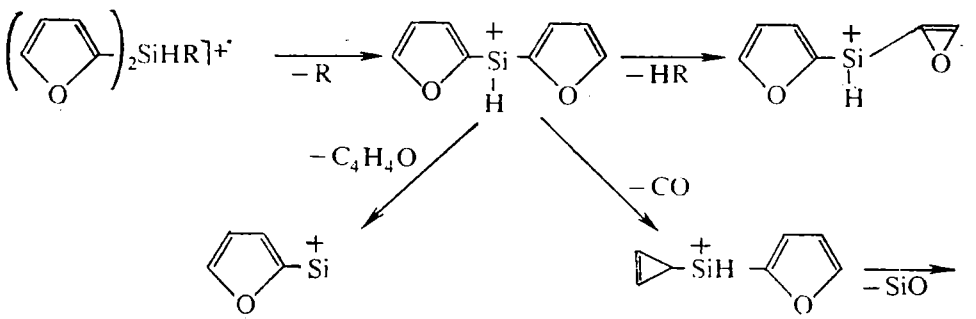
Homolytic breakdown of the Si—R bond is a common event during decomposition of the molecular ions of 2-furylsilane derivatives of the  type. Because the charge is delo-

calized over the conjugated system of the furan cycle, the furyl radical is not detached. After this, the (M—R)+ ion eliminates the molecule of acetylene and also the alkane molecule:

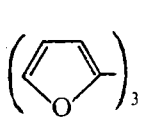
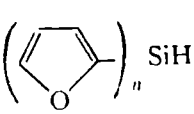


(20)

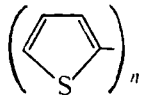
Similarly, di(2-furyl)silane derivatives of the  type begin decomposing when the Si—R bond breaks down; this event is followed by the parallel elimination of furan, acetylene, and carbon monoxide molecules followed by rearrangement and formation of tropylium ion:



(21)

The presence of the second furyl substituent slightly stabilizes the molecular ion because of delocalization of the unpaired electron over two furan cycles. Mass-spectrometric decomposition of tri(2-furyl)-silane derivatives of the  type also involves the primary detachment of substituent R. The magnitudes of the ratios of intensities, I_M/I_{M-R}, for compounds of the  type indicate that the stability of the molecular ion grows as the number of furyl groups increases; the dependence of the ratio on n is described by the following equation [21]:

$$\log I_M/I_{M-R} = -0.44 + 0.46n \quad r = 0.997 \quad n = 1\text{-}4$$

In the mass spectra of 2-thienyl(chloromethyl)silanes derivatives of the  ($X = H, Me, OEt, Cl$; $n = 1-3$) type the highest peaks are generated by ions formed as a result of the detachment of the chloromethyl radical [25]. Later on, the detachment of substituents X, thiophene molecules, the destruction of the thiophene ring, and the elimination of the acetylene molecules occur.

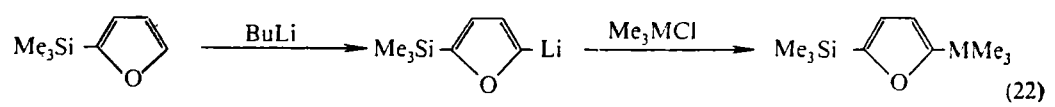
3.6. X-Ray Structure Analysis

The furan and thiophene heterocycles in 1-(2′-furyl)-, 1-(3′-furyl)-, 1-(2′-thienyl)-, and 1-[β-dimethyl(2′-furyl)silylethyl]-silatranes have a flat structure [4, 74]. Bond lengths in these heterocycles do not exceed the limits of usual values [74]. The Si ← N interatomic distance in 1-(2′-furyl)-, 1-(2′-thienyl)-, and 1-[β-dimethyl(2′-furyl)silylethyl]silatranes is 2.11, 2.13, and 2.23 Å, respectively.

4. CHEMICAL PROPERTIES

All known reactions for organosilicon derivatives of furan and thiophene can be classed into three types: transformations of the heterocycle and substituents linked to it, substitution of functional groups at the silicon atom, and splitting of the bond between the silicon and the furan or thiophene ring. The latter reaction often accompanies the processes that involve basic or acidic reactants.

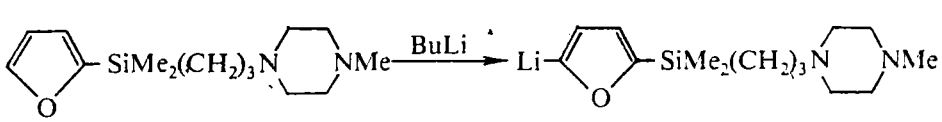
The direction of the reaction of Si-substituted furylsilanes with butyl lithium is determined by their structure [75]. Thus, metallation of trimethyl(2-furyl)silane (in position 5) is accompanied by detachment of the trimethylsilyl group [76]. The thus formed lithium derivatives are used for obtaining 2,5-disubstituted derivatives of furan [3, 31, 32]:



(22)

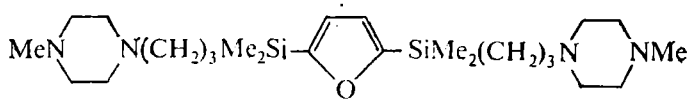
The reaction of methyltri(2-furyl)silane and tetra(2-furyl)silane with butyl lithium in THF proceeds with the splitting of the Si—C bond [75, 76].

Two reaction sites participate in the reaction between butyl lithium and dimethyl[3-(N-methylpiperazino)propyl] (2-furyl)silane [21, 76]:

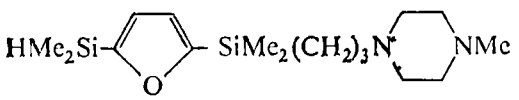


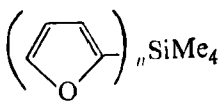
(23)

The lithium derivative formed in this reaction then reacts with a molecule of the initial organosilicon derivative, affecting the Si-furyl bond and giving

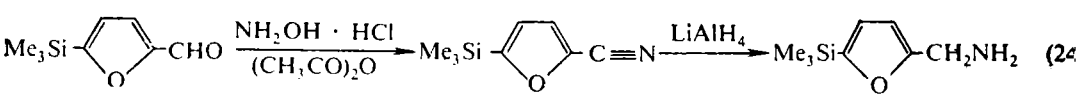


Interaction of this same lithium derivative with dimethylchlorosilane results in the formation of

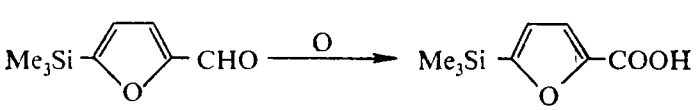


Methyl(2-furyl)silanes  can be nitrated with acetyl nitrate in acetic anhydride and halogenated alkanes at temperatures between —30 and —20 °C [77]. Nitration of trimethyl(2-furyl)silane gives trimethyl(5-nitro-2-furyl)silane, insignificant amounts of trimethyl(4-nitro-2-furyl) silane, and also desilylation products and 2,5-dihydrofuran derivatives. Under these conditions, tetra(2-furyl)silane is the most stable: its nitration proceeds with the formation of tetra(5-nitro-2-furyl)silane.

Trimethylsilyl derivatives of furan that have different functional groups in the ring were obtained from 5-(trimethylsilyl)furfural. This compound interacts with hydroxylamine hydrochloride and acetic anhydride in pyridine to give 5-(trimethylsilyl-2-cyano)furan in a 92% yield; the latter, in turn, can be easily reduced with lithium alumohydride in ether to 5-(trimethylsilyl)furfurylamine [30, 78]:



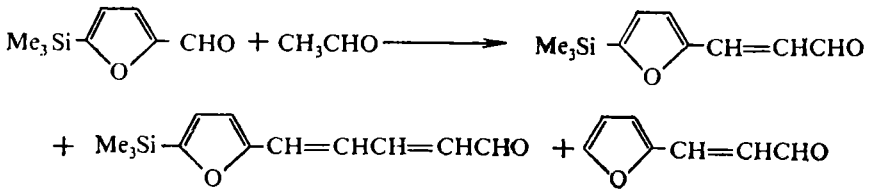
The oxidation of 5-(trimethylsilyl)furfural with silver oxide or potassium permanganate leads to the formation of a corresponding acid:



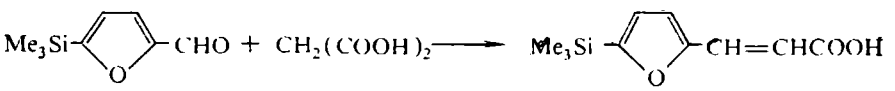
(25)

The condensation of 5-(trimethylsilyl)furfural with acetic aldehyde and malonic acid in the presence of bases follows these schemes:

[30, 78]:

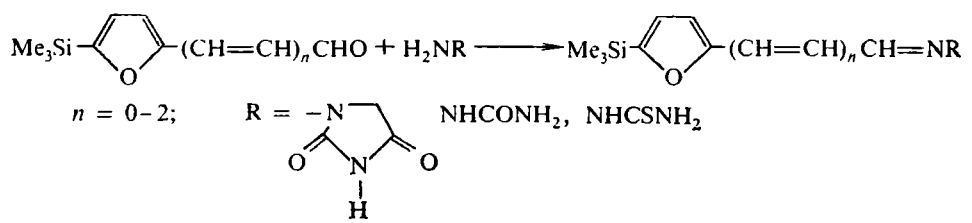


(26)



(27)

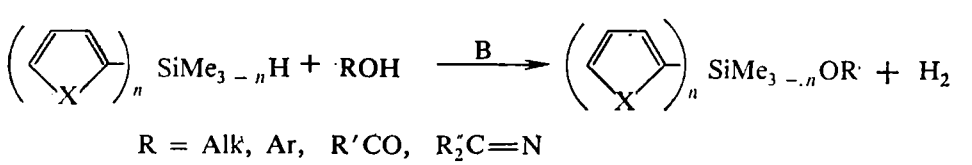
The trimethylsilyl group is partly detached in the first case. 5-Trimethylsilyl derivatives of furfural, furylacrolein, and furylpentadienal have been condensed with aminohydantoin, semicarbazide, and thiosemicarbazide in alcohol or water-alcohol medium [78]. The yield of the reaction products was 56-96%. Detachment of the trimethylsilyl group was not observed:



(28)

The functional groups at the silicon in the derivatives of 2-furyl- and 2-thienylsilane easily enter various exchange reactions.

The chemical properties and reactivity of furyl- and thienylhydrosilanes have been studied most extensively. These compounds easily enter into hydrocondensation with different hydroxy compounds in the presence of chloroplatinic acid [1-3, 6, 15], organic bases [79-91] and in the case of tri(2-furyl)silane [3], without a catalyst. An analysis of the kinetics of the reaction



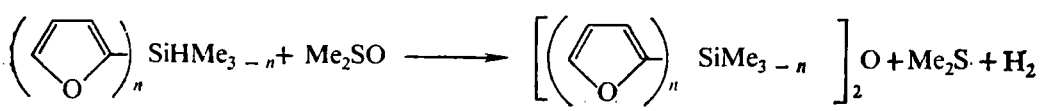
(29)

has shown that the reactivity of alkanols [79, 82, 85, 88], phenols [79, 80, 87], and oximes [79, 84] grows as the $-I$ effect of the substituent that is linked to the hydroxyl group increases. The presence of an electron-acceptor substituent in the molecule of a carboxylic

acid reduces its activity in the dehydrocondensation reaction. Depending on the nature of substituents at the silicon atom, the rate of dehydrocondensation of triorganylsilanes of the $R_2R'SiH$ type decreases in the following R series: 2-furyl > 2-thienyl > phenyl > > 2-(4,5-dihydrofuryl) > 3-furyl [79, 91]. The reactivity grows as the number of heterocyclic substituents at the silicon does. The spin-spin interaction constants, J_{SiH}, are most sensitive to structure changes in $R_2R'SiH$ molecules. They show a satisfactory correlation with the rate constant logarithms of their dehydrocondensation with propargyl alcohol [79]:

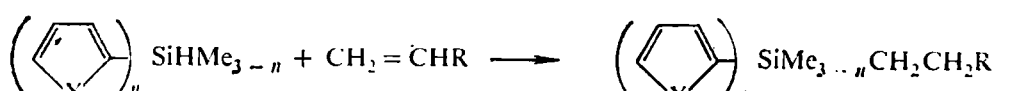
$$\log k = -33.5 + 0.17^1 J_{SiH} \qquad (30)$$

Methyl(2-furyl)hydrosilanes easily reduce dimethylsulphoxide in the presence of H_2PtCl_6 [92, 93]:



(31)

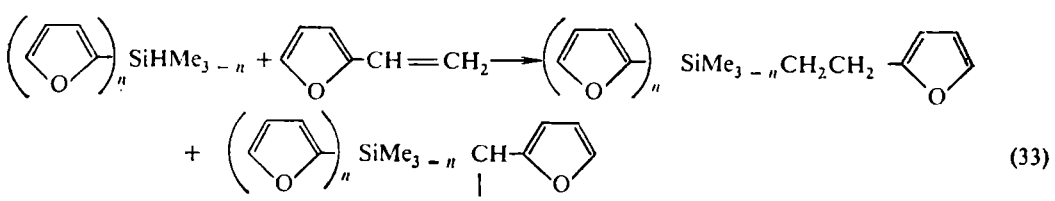
Methyl(2-furyl)- or methyl(2-thienyl)hydrosilanes are highly active during hydrosilylation of unsaturated compounds in the presence of Speier's catalyst:



$n = 1-3$; X = O, S;

R′ = CH_2NR_2 [4, 24, 28, 94–96], $CH_2ON{=}CMe_2$ [95], $SiEt_3$ [2, 6], $Si(OCH_2CH_2)_3N$ [4, 24, 28] (32)

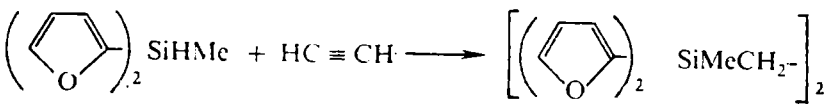
In most cases, hydrosilylation of vinyl derivatives yields one adduct. However, hydrosilylation of 2-vinylfuran by methyl(2-furyl)hydrosilanes results in the formation of two isomeric addition products:



(33)

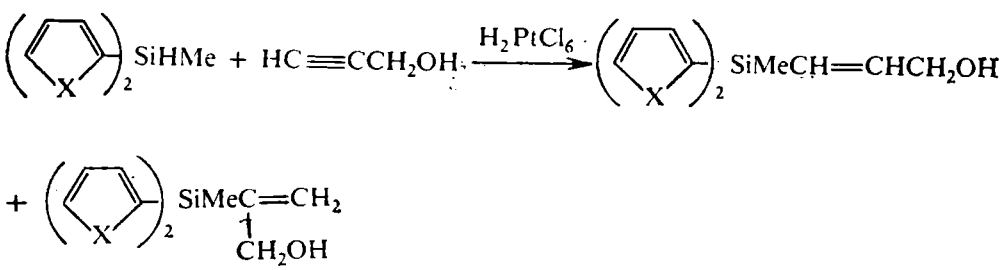
The proportion of the β isomer increases as the number of furyl groups at the silicon does (84, 90, and 94% for n = 1, 2, and 3, respectively) [28, 95].

The reaction of methyldi(2-furyl)silane with acetylene is exothermal and follows mostly this scheme [29, 95, 96]:



(34)

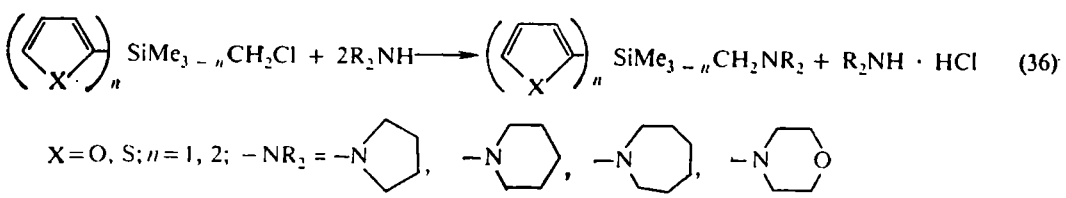
Methyldi(2-furyl)- [28, 95, 97] and methyldi(2-thienyl)silane [79] already begin to react with propargyl alcohol while the reactants are mixed and form two isomeric adducts:



(35)

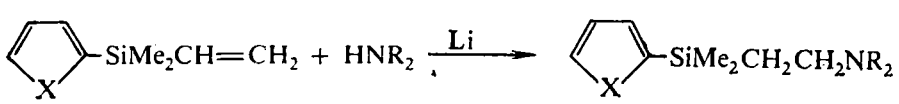
The hydroxyl is not involved under these conditions. At the same time, in the presence of organic amines, only dehydrocondensation takes place [79].

At 70 °C, methyl(2-furyl)- and methyl(2-thienyl)chloromethylsilanes react with amines to give the corresponding amino derivatives (50-60% yield) [4, 24, 96]:



(36)

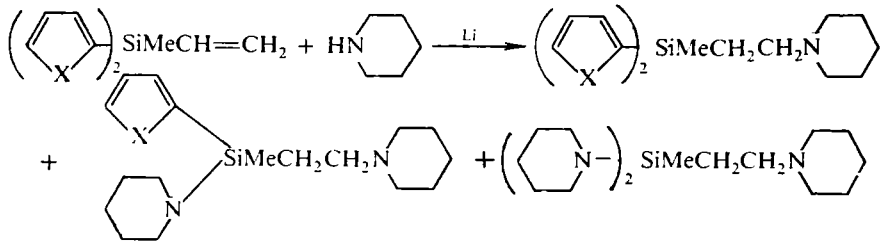
Dimethyl(2-furyl)- and dimethyl(2-thienyl)vinylsilanes react with secondary heterocyclic amines in THF at 70 °C (in the presence of catalytic amounts of metallic lithium) to furnish corresponding β-aminoethyl derivatives [4, 24, 96]:



(37)

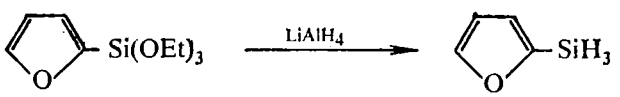
A similar reaction of methyldi(2-furyl)- and methyldi(2-thienyl)-vinylsilanes is accompanied by the detachment of one heterocyclic

substituent:



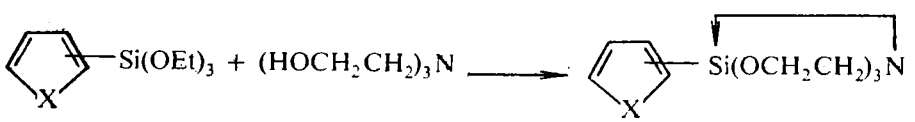
(38)

2-Furyltriethoxysilane is reduced by lithium alumohydride in ether at —20 °C to 2-furylsilane [21, 22, 29]:



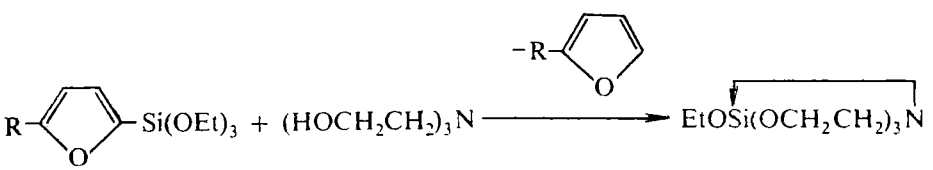
(39)

Transesterification reaction between heteryltrialkoxysilanes and triethanolamine in xylene produces corresponding silatranes [4, 19, 23, 26, 53, 98, 99]:



(40)

2-Furyltriethoxysilane interacts with triethanolamine without any catalyst to give 1-(2′-furyl)silatrane in a 76% yield. The use of chloroplatinic acid as catalyst increases the yield by 12%. In the presence of alkali hydroxides, the usual transesterification catalysts, interaction between 2-furyl- or 5-methyl-2-furyltriethoxysilane and triethanolamine involves the cleavage of the Si—C bond and the formation of 1-ethoxysilatrane [4, 26, 53]:

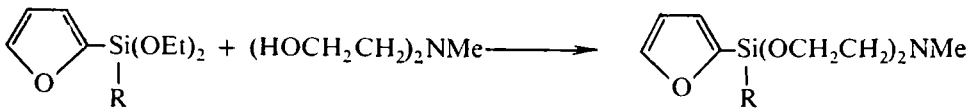


(41)

Compounds in which the silatrane skeleton is separated from the furan heterocycle by one or two methylene groups or occupies position 3 in the furan or thiophene ring [4, 53] are formed in transesterification reactions of corresponding organyltriethoxysilanes in the presence of a basic catalyst.

Corresponding derivatives of 1,3-dioxo-6-aza-2-silacyclooctane arise as a result of (2-furyl)triethoxy- and di(2-furyl)diethoxysi-

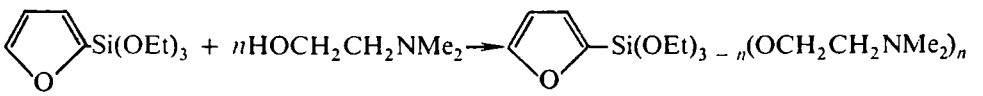
lanes reacting with N-methyldiethanolamine [4, 53]:



(42)

R = EtO. 2-furyl

2-Furyltriethoxysilane interacts with N,N-dimethylethanolamine (1:1 and 1:3 molar ratios) with the substitution of one or correspondingly all three ethoxy groups [4, 53]:



(43)

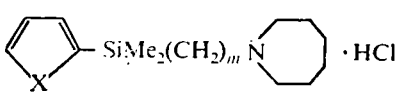
The hydrolysis of trialkoxysilylmethyl esters of 3-(2-furyl)acrylic acid or their cohydrolysis with organyltrialkoxysilanes produces light-sensitive organosilicon resins cured under UV light [100, 101]. Tetrafurfuryloxysilane undergoes polymerization in the presence of acid catalysts and forms acid-resistant resins that are stable when heated to 400-450 °C [42].

5. BIOLOGICAL ACTIVITY

Compounds featuring high biological activity have been found among furan and thiophene derivatives of silicon. Their psychotropic effect has been studied most extensively. The effect of the nature of substituents at the silicon and nitrogen on psychotropic activity and the position of the amino group with respect to the silicon in (aminoalkyl)(2-furyl)- and (aminoalkyl)(2-thienyl)silanes and in their hydrochlorides was investigated [4, 24, 94, 102-105].

The administration of compounds of this type to white mice and rats results in a certain sedative effect. An increase in the number of 2-furyl groups in (3-aminopropyl)(2-furyl)silanes slightly lowers their toxicity but also reduces their activity [94].

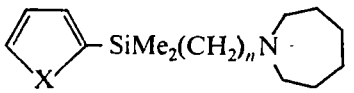
In the series of perhydroazepine derivatives 2-furyl- and in 2-thi-



enylsilane showed the highest activity in the "tube" and "rotating rod" tests. They have the silicon and nitrogen separated by two methylene groups [4, 24] (Table 3). Thienylsilane derivatives are less toxic than their furyl analogues.

Of the 2-R-$(CH_2)_nSi(OCH_2CH_2)_3N$ compounds (R = 2-furyl- or 2-thienyl-), the highest acute toxicity is manifested by compounds with n = 0 (Table 4) [4, 17, 98, 103, 106]. The lethal dose of

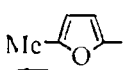
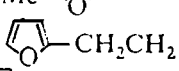
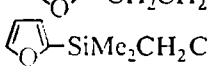
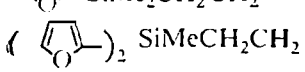
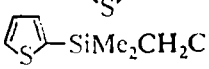
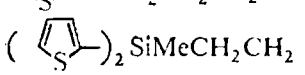
Table 3. Pharmacological Activity of



· HCl in Experiments on BALB/c Strain Mice on Intraperitoneal Administration

X	*m*	LD_{50}, mg/kg	ED_{50}, mg/kg	
			"tube" test	"rotating rod" test
O	1	78	9	9
O	2	72	6	6
O	3	70	14	13
S	1	125	26	26
S	2	115	5	5
S	3	110	28	28

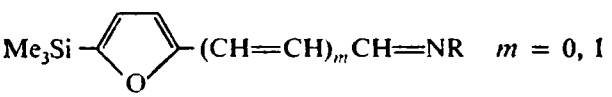
Table 4. Pharmacological Activity of Silatranes, $\overset{\downarrow}{R}Si(OCH_2H_2)_3\overset{\uparrow}{N}$, in Experiments on Mice on Intraperitoneal Administration

R	LD_{50}, mg/kg	ED_{50}, mg/kg	
		"tube" test	"rotating rod" test
	125	14.5	14.5
	14.5	1.5	1.5
	2100	10	10
	235	16	14
	700	20	14
	2450	92	92
	0.3	0.0016	0.0016
	1.8	0.0016	0.0016
	1650	92	92
	3900	150	150

1-(2′-thienyl)silatrane is comparable with that of phenylsilatrane [98, 99, 4, 17, 98, 99, 106]. At the same time, the toxicity of 1-(2′-furyl)-silatrane is about 1/400 of the toxicity of phenylsilatrane. Its neurotropic activity is also lower. The pharmacological effect of 2-heteryl- and 3-heterylsilatranes is just the opposite. Thus, 1-(3′-furyl)- and 1-(3′-thienyl)silatranes act to sedate animals, reduce their motorial activity, and relax their skeletal muscles; on the other hand, 1-(2′-furyl)- and 1-(2′-thienyl)silatranes act as stimulants [4, 17].

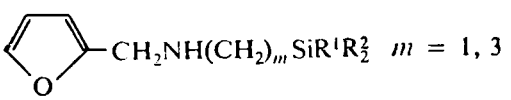
Introducing a methyl group at position 5 in the furan ring of 1-(2′-furyl)silatrane greatly reduces its acute toxicity [4, 17], while a similar change in the thiophene series lowers the LD_{50} value [98, 99].

5-Substituted derivatives of (2-trimethylsilyl)furan, such as



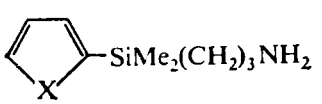
have a clearly expressed antitumour effect in Lewis' lung carcinoma and B_{16} melanoma (tumour growth retardation to 60%). Ehrlich's ascitic tumour and sarcoma 37 are less sensitive to these compounds [107].

Organosilicon derivatives of furfurylamine [108, 109] of the



type effectively suppress many strains of pathogenic fungi. Compounds with R^1 = Me, R^2 = Bu have been predicted to have high activity [109].

Methyl(2-furyl)- and methyl(2-thienyl)(3-aminopropyl)silanes



are slightly active with respect to wheat rust, Phytophthora rot of tomatoes, and cucumber powdery mildew [110].

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9 Trimethylsilyl Ethers of Methylolamines and Methylolamides

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1. INSERTION OF FORMALDEHYDE INTO THE Si—N BOND

At the time we embarked on our studies in 1981, no mention could be found in the literature regarding the interaction of formaldehyde with compounds containing a Si—N bond.

1.1. Synthesis of Trimethylsilyl Ethers of Methylolamines

The general reaction we discovered between gaseous formaldehyde and diorganyl(N-trimethylsilyl)amines [1-8] lacking N—H bonds proceeds as follows:

$$\underset{\text{I}}{RR'NSiMe_3} + CH_2O \xrightarrow{20-150\ ^\circ C} \underset{\text{II}}{RR'NCH_2OSiMe_3} \qquad (1)$$

R = R′ = Me (a); R = R′ = Et (b); R = R′ = Bu (c);
R = R′ = Ph (d); R = R′ — $PhCH_2$ (e);
R = R′ = CH_2=CH—CH_2 (f); R = CH_2=CH—CH_2, R′ = Bu (g);
RR′ = —$(CH_2)_5$— (h); RR′ = —$CH_2CH_2OCH_2CH_2$— (i)

The concomitant insertion of formaldehyde into the Si—N bond results in the formation of trimethylsilyl ethers of methylolamines (II) that were previously unknown. Reaction (1) is highly exothermic, its rate and thermal effect increase with the nucleophility of I. It is accompanied by a condensation reaction that follows scheme (2). This condensation becomes particularly pronounced in the case of highly nucleophilic amines (Ic-Ie):

$$\underset{\text{I}}{RR'NSiMe_3} + \underset{\text{II}}{RR'NCH_2OSiMe_3} \rightarrow \underset{\text{III}}{RR'NCH_2NRR'} + (Me_3Si)_2O \qquad (2)$$

The temperature at which the process is conducted has a great effect on the relative yield of products II and III: reactions (1) and (2). As a rule, decreasing temperature enhances the yield of II. For example, the yield of IIb increases from 40 to 70% when the temperature drops from 90-110 to 30-35 °C.

Bis-, tris-, and tetrakis(dialkylamino)silanes $R_nSi(NR'_2)_{4-n}$ (n = 0, 1, 2) react with formaldehyde in the same vigorous manner. Excess formaldehyde yields products of insertion into all Si—N bonds. In particular, vinyl-tris(diethylamino)silane combines with CH_2O to form a 1:3 adduct, viz. vinyl-tris(diethylaminomethoxy)silane, $CH_2=CHSi(OCH_2NEt_2)_3$ in a yield close to quantitative.

The reaction of formaldehyde with a mixture of secondary amine and hexamethyldisilazane at 50-55 °C also yields II.

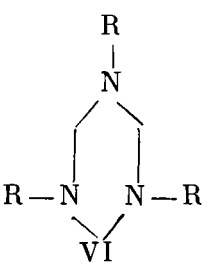
$$Et_2NH + (Me_3Si)_2NH + CH_2O \rightarrow$$
$$\rightarrow \underset{\text{IIb}}{Et_2NCH_2OSiMe_3} + \underset{\text{IIIb}}{Et_2NCH_2NEt_2} + (Me_3Si)_2O + NH_3 \qquad (3)$$

When α-polyoxymethylene is used as a source of gaseous formaldehyde, better yields of insertion products are achieved than in the case of paraform.

Trimethylsilyl ethers II are colourless mobile liquids which lend themselves readily to vacuum distillation. However, when heated (at 100 °C) or stored over a long period of time, they may dissociate back into the starting reactants.

Organyl(N-trimethylsilyl)amines IV also react with formaldehyde in an exothermic manner, yielding 1,3,5-triorganylhexahydro-1,3,5-triazines (VI) and hexamethyldisiloxane:

$$\underset{\text{IV}}{RNHSiMe_3} + CH_2O \rightarrow \underset{\text{V}}{[RNHCH_2OSiMe_2]} \xrightarrow[-Me_3SIOH]{} \rightarrow [RN=CH_2] \rightarrow 1/3$$



$$\qquad (4)$$

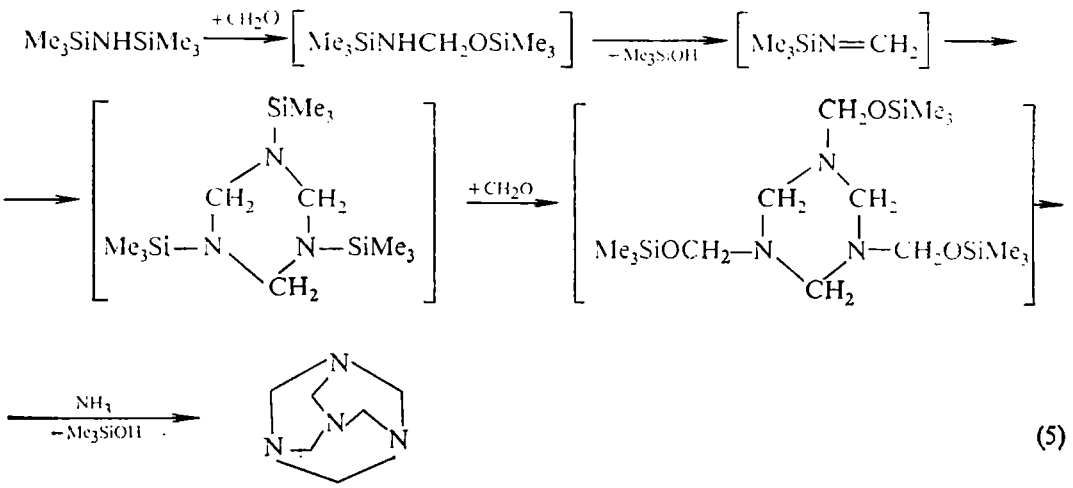
VI

R = Me (a); R = $CH_2=CH-CH_2$ (b); R = Bu (c)

The different reactivity of tertiary (I) and secondary (IV) amines stems from their tendency for β-elimination of labile 1:1 adducts (V). Their formation at —5 to —50 °C has been proven by ^1H NMR and IR spectroscopy.

As one goes from $RNHSiMe_3$ (IV) to $Me_3SiNHSiMe_3$ whose nitrogen has lower nucleophility, the reactivity of the Si—N bond in respect to formaldehyde decreases drastically. For example, hexamethyldisilazane does not react with formaldehyde at temperatures up to 100 °C without a catalyst and a solvent. Instead, formaldehyde undergoes polymerization, and polyformaldehyde is partially silylated at the terminal OH groups. However, in the presence of dimeth-

ylformamide or a catalytic amount of Et_3N or Me_3SiONa, the reaction product is urotropin (VII) in 80% yield. This indicates that formaldehyde is inserted into both Si—N bonds of hexamethyldisilazane in the above conditions. This reaction seems to proceed as follows:



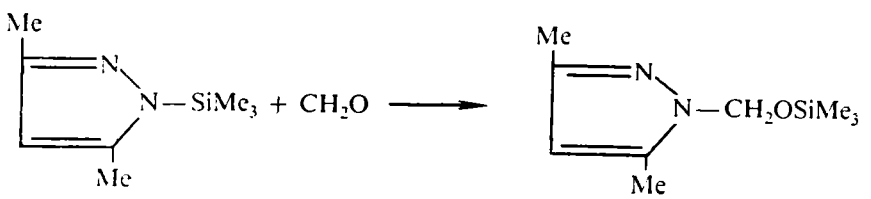
(5)

VII

Formaldehyde is inserted into the Si—N bond of N-alkylhexamethyldisilazanes only at temperatures above 100 °C. The reaction yields a product of the insertion of two formaldehyde molecules (IX). This can be explained by the higher nucleophility of the nitrogen in the intermediate 1:1 adduct (VIII), as compared with the starting heptamethyldisilazane:

$$MeN(SiMe_3)_2 + CH_2O \longrightarrow \underset{\text{VIII}}{[MeN(CH_2OSiMe_3)SiMe_3]} \xrightarrow{+CH_2O} \rightarrow \underset{\text{IX}}{MeN(CH_2OSiMe_3)_2} \quad (6)$$

N-(Trimethylsilyl)azoles, such as 3,5-dimethyl-N-(trimethylsilyl)-pyrazole, readily reacts with formaldehyde at 100 °C, forming the insertion product with the yield more than 80%:



(7)

This(trimethylsilyl)amine ' and N,N'-bis(trimethylsilyl)carbodiimide do not react with formaldehyde up to 150 °C, even in the presence of a catalytic amount of Me_3SiONa.

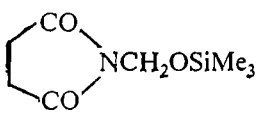
1.2. Synthesis of Trimethylsilyl Ethers of Methylolamides

Silylated primary and secondary amides of carboxylic acids (X) react exothermally with formaldehyde in the absence of a catalyst and a solvent to produce trimethylsilyl ethers of N-methylolamides (XI)* in high yields [6, 7]:

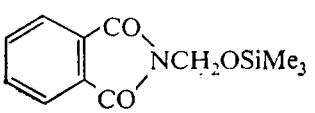
$$\underset{\text{X}}{RCONR'SiMe_3} + CH_2O \rightarrow \underset{\text{XI}}{RCONR'CH_2OSiMe_3} \quad (8)$$

R = R′ = H (a); R = Me, R′ = H (b); R = R′ = Me (c);
R = Me, R′ = CH(CH$_3$)$_2$ (d)

N-(Trimethylsilyl)succinimide and N-(trimethylsilyl)phthalimide do not react with formaldehyde without a catalyst at 20-30 °C. Yet, in the presence of Me_3SiONa (abt. 1 mol.%) or at temperatures above 100 °C, they yield large amounts of respective N-(trimethylsiloxymethyl)imides (XII) and (XIII).



XII



XIII

N-(Trimethylsilyl)lactams (derivatives of pyrrolidone and caprolactam) readily react with formaldehyde at 100 °C, yielding sizable amounts of similar insertion products. At 20 to 60 °C, the reaction is slow, and is accompanied by significant polymerization of formaldehyde.

It is known, that unlike mono- and disubstituted ureas, trialkylureas do not react with formaldehyde in acidic or alkaline media [10]. Trimethylsilylation of trialkylureas sharply increases their reactivity in respect to formaldehyde [8]. For instance, trialkyl(trimethylsilyl)ureas (XIV) react exothermally with formaldehyde, forming stable trimethylsilyl ethers of trialkyl(methylol)ureas (XV):

$$\underset{\text{XIV}}{RR'N-CO-NMeSiMe_3} + CH_2O \rightarrow \underset{\text{XV}}{RR'N-CO-N(Me)CH_2OSiMe_3} \quad (9)$$

R = R′ = Me (a); R = R′ = Et (b)

N-(Trimethylsilyl)urethanes react with formaldehyde much more reluctantly than N-(trimethylsilyl)amides of monocarboxylic acids. For instance, when formaldehyde was passed through $Me_3SiNRCOOR'$ (R = H, CH_2=CH—CH_2; R′ = Me, Et) at 20-80 °C in the presence

* Some compounds of this type were obtained earlier by silylation of the methylol derivatives of amides [9].

of up to 1 mol.% Me_3SiONa, only the starting N-(trimethylsilyl)-urethanes were yielded. The reaction was found to yield a small amount of the product of insertion of formaldehyde into the Si—N bond only in the case of $CH_2=CH—CH_2(Me_3Si)NCOOMe$ (according to ^1H NMR and IR spectroscopy).

Bis(trimethylsilyl)amides of carboxylic acids (XVI) combine with only one formaldehyde molecule between 50 and 130 °C. This is another proof of the imidate structure of these compounds:

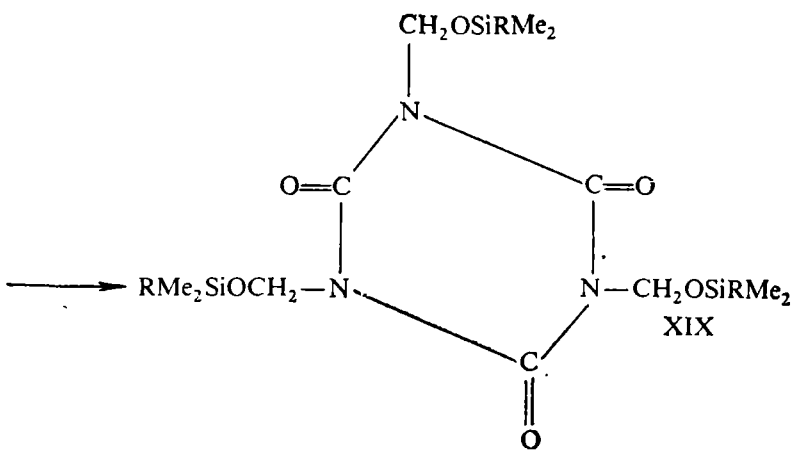
$$\underset{\text{XVI}}{RC(OSiMe_3)=NSiMe_3} + CH_2O \rightarrow RC(OSiMe_3)=NCH_2OSiMe_3 \qquad (10)$$

R = Me (a); R = Ph (b)

1.3. Reactions between Formaldehyde and Triorganylisocyanatosilanes

The reactivity of the Si—N bond in triorganylisocyanatosilanes is lower than in all of the previously discussed compounds. They react with formaldehyde only in the presence of a catalytic amount of a base, such as Et_3N. Without a catalyst, the reaction does not take place even at temperatures ranging from 100 to 150 °C. The primary insertion products, triorganylsiloxymethylisocyanates (XVIII), are sometimes trimerized into respective 1,3,5-tris(triorganylsiloxymethyl)isocyanurates (XIX) [6]:

$$\underset{\text{XVII}}{RMe_2SiNCO} + CH_2O \xrightarrow{Et_3N} \underset{\text{XVIII}}{[RMe_2SiOCH_2NCO]} \rightarrow$$



(11)

XIX

R = Me (a); R = Ph (b); R = CH_2=CH (c); R = $ClCH_2$ (d)

Thus, between 100 to 105 °C, $Me_2PhSiNCO$ yields primarily the monomeric XVIIIb, whereas the reaction between CH_2O and XVIIa, c, d yields only the corresponding isocyanurates XIX.

Heating $Me_2PhSiNCO$ for three hours with paraformaldehyde at 150 °C also results in isocyanate XVIIIb. The same reaction in the presence of a catalytic amount of Et_3N yields mainly trimer XIXb.

In the presence of chlorosilanes, which are essentially stabilizers of organic isocyanates, formaldehyde undergoes vigorous polymerization.

Isocyanurates XIX were previously unknown. They are slowly hydrolyzed in air and are thermally unstable. Their thermal decomposition leads to elimination of formaldehyde. For example, XIXa decomposes, when heated, to CH_2O and Me_3SiNCO rather than to XVIIIa as would be the case with organic isocyanurates.

2. CHEMICAL PROPERTIES OF TRIMETHYLSILYL ETHERS OF METHYLOLAMINES AND METHYLOLAMIDES

Trimethylsilyl ethers of methylolamines and methylolamides differ from trimethylalkoxysilanes by their high reactivity in respect to nucleophylic reagents. They react exothermally with chlorosilanes, isocyanates, and with some other compounds with which trimethylalkoxysilanes are inert. The reactions involving these compounds are accompanied by cleavage of the C—O bond, while in the case of trimethylalkoxysilanes it is the Si—O bond that cleaves most often.

2.1. Hydrolysis and Alcoholysis

When trimethylsilyl ethers of methylolamines, methylolamides, and methylolazoles are exposed to water or alcohols, they are desilylated to yield the corresponding methylol derivatives. The latter (with the exception of amide derivatives) are not stable and eliminate formaldehyde:

$$\text{>NCH}_2\text{OSiMe}_3 + \text{ROH} \xrightarrow[-\text{ROSiMe}_3]{} \text{>NCH}_2\text{OH} \rightarrow \text{>NH} + \text{CH}_2\text{O} \qquad (12)$$

R = H, CH_3, C_2H_5

According to ^{1}H NMR and IR spectroscopy, the hydrolytic stability of N-trimethylsiloxymethyl derivatives of nitrous bases increases in the following order: amines < azoles < amides ≃ ureas.

Attempts to obtain methylol derivatives of trialkylureas by mild hydrolysis of their trimethylsilyl ethers at different pH values have not been successful. The parent trialkylureas were all that resulted from this hydrolysis [8]:

$$\text{RR'NCON(Me)CH}_2\text{OSiMe}_3 + \text{R''OH} \xrightarrow[-\text{R''OSiMe}_3]{}$$

$$\rightarrow [\text{RR'NCON(Me)CH}_2\text{OH}] \rightarrow \text{RR'NCONHMe} + \text{CH}_2\text{O} \qquad (13)$$

R = R' = Me (a); R = R' = Et (b); R'' = H, Me, Et

2.2. Reactions with the N-Trimethylsilyl Derivatives of Secondary and Primary Amines

We have succeeded in extending what was mentioned as a side reaction (2) to cover N-trimethylsiloxymethyl derivatives of various nitrous bases (amines, azoles, amides, and lactams). We have also demonstrated that it can be used as a source of the corresponding derivatives of methylenediamine [11]:

$$\underset{\text{XX}}{R_2NCH_2OSiMe_3} + \underset{\text{XXI}}{Me_3SiNR'_2} \rightarrow \underset{\text{XXII}}{R_2N-CH_2-NR'_2} + (Me_3Si)_2O \qquad (14)$$

R = R′ = Me (a); R = R′ = Et (b); $R_2 = R'_2 = (CH_2)_5$ (c);

$R_2 = R'_2 = O(CH_2-CH_2)_2$ (d); $R_2 = R'_2 = C(Me)=CH-C(Me)=N$ (e);

R = Me, R′ = Et (f); R = Et, R′ = $CH_2=CH-CH_2$ (g);

R = $CH_2=CH-CH_2$, R′ = Et (h); R = Et, $R'_2 = C(Me)=CH-C(Me)=N$ (i);

R = Et, NR'_2 = NHC(O)Me (j);

R = Et, $R'_2 = CH_2(CH_2)_4C(O)$ (k); $NR_2 = NR'_2$ = NHC(O)Me (l)

Reaction (14) becomes more facile as the nucleophility of the starting substances increases. For instance, the reaction of N-(trimethylsiloxymethyl)piperidine (XXc) with N-(trimethylsilyl)piperidine (XXIc) even at subzero temperatures yields bis(N-piperidyl)methane (XXIIc). The same facility was observed in reactions involving similar derivatives of morpholine (XXd, XXId). Derivatives of 3,5-dimethylpyrazole (XXe, XXIe) are not reactive even at 150 °C. However, in the presence of a catalytic amount of $AlCl_3$, bis(N-3,5-dimethylpyrazolyl)methane (XXIIe) is formed in a virtually quantitative yield. Catalytic properties are also displayed by other Lewis acids ($ZnCl_2$, $SnCl_4$, or $TiCl_4$).

Reactions involving XX and XXI with dissimilar substituents at the nitrogen atom may be complicated by transamination. For example, on heating of dimethyl(trimethylsiloxymethyl)amine together with diethyl(trimethylsilyl)amine, which is accompanied by distillation of the resulting Me_2NSiMe_3 and $(Me_3Si)_2O$. The reaction proceeds along two routes:

$$Me_2NCH_2OSiMe_3 + Et_2NSiMe_3 \begin{cases} \rightarrow Et_2NCH_2OSiMe_3 + Me_2NSiMe_3 \\ \rightarrow Me_2NCH_2NEt_2 + (Me_3Si)_2O \end{cases} \qquad (15)$$

Along with the elimination of hexamethyldisiloxane, transamination also involves a partial reaction of $Et_2NCH_2OSiMe_3$ with $(CH_2=CH-CH_2)_2NSiMe_3$ or Ph_2NSiMe_3. However, neither $Me_2NCH_2OSiMe_3$ nor $Et_2NCH_2OSiMe_3$ react with N-trimethylsilylsubstituted azoles, lactams, and amides when heated. In general, transamination reaction is characteristic of diorganyl(trimethylsiloxymethyl)-amines (XX) with alkyl (but not with acyl) substituents at the

nitrogen atom. Besides the reaction between $R_2NCH_2OSiMe_3$ and $R_2N'SiMe_3$ occurs only when R′ is a more bulky substituent as compared with R. The reaction of diethyl(trimethylsiloxymethyl)amine with diallyl(trimethylsilyl)amine is accompanied by transamination:

$$\begin{aligned} &Et_2NCH_2OSiMe_3 + \\ &+(CH_2=CH-CH_2)_2NSiMe_3 - \begin{cases} \rightarrow (CH_2=CH-CH_2)_2NCH_2OSiMe_3 + Et_2NSiMe_3 \\ \rightarrow Et_2NCH_2N(CH_2=CH-CH_2)_2 + (Me_3Si)_2O \end{cases} \end{aligned} \qquad (16)$$

At the same time, the reaction between diallyl(trimethylsiloxymethyl)amine and diethyl(trimethylsilyl)amine proceeds only as in (14).

The reaction of $Et_2NCH_2OSiMe_3$ with $BuNHSiMe_3$ yields hexamethyldisiloxane and 1,3,5-tributylhexahydro-1,3,5-triazine(XXVI). It seems to proceed with intermediate formation of condensation (XXIII) or transamination (XXIV) products whose β-decay leads to N-butylmethylenimine (XXV) which is then trimerized to XXVI:

$$Et_2NCH_2OSiMe_3 + BuNHSiMe_3 - \left[\begin{array}{l} \xrightarrow[-(Me_3Si)_2O]{} Et_2NCH_2NHBu \xrightarrow[-Et_2NH]{} \\ \qquad\qquad XXIII \\ \xrightarrow[-Et_2NH]{} BuNCH_2OSiMe_3 \xrightarrow[-(Me_2Si)_2O]{} \\ \qquad\qquad | \\ \qquad\qquad SiMe_3 \\ \qquad\qquad XXIV \end{array} \right] \rightarrow$$

$$\rightarrow \underset{XXV}{[BuN=CH_2]} \rightarrow 1/3 \quad \underset{XXVI}{\text{Bu-substituted triazine}} \qquad (17)$$

2.3. Reactions with Trialkylhalogenosilanes

Trimethylsilyl ethers of dialkyl(methylol)amines easily eliminate hexamethyldisiloxane also when they react with trialkylhalogenosilanes [11]:

$$\underset{II}{R_2NCH_2OSiMe_3} + XSiR'_3 \rightarrow [R_2\overset{+}{N}=CH_2][X^-] + Me_3SiOSiR'_3 \qquad (18)$$

R = Me, Et; R′ = Me, Et; X = Cl, Br, I

The reaction is exothermic in the absence of a solvent or in ether, and produces a high yield of the respective hexaalkyldisiloxane and dialkyl(halogenmethyl)amine (in the form of an ammonium salt). The latter are valuable and hard to obtain aminomethylating synthones, and their synthesis in this manner has a number of advantages over the existing procedures [12].

N-(Trimethylsiloxymethyl)acetamide reacts with Me_3SiCl at 40-60 °C with a quantitative yield of N-(chloromethyl)acetamide and hexamethyldisiloxane:

$$MeCONHCH_2OSiMe_3 + ClSiMe_3 \rightarrow MeCONHCH_2Cl + (Me_3Si)_2O \quad (19)$$

Trialkyl(trimethylsiloxymethyl)ureas form trialkyl(chloromethyl) ureas which are potentially effective amidomethylating agents:

$$RR'NCON(Me)CH_2OSiMe_3 + Me_3SiCl \rightarrow$$
$$\rightarrow RR'NCON(Me)CH_2Cl + (Me_3Si)_2O \quad (20)$$
$$R = R' = Me \text{ (a)}; \quad R = R' = Et \text{ (b)}$$

1,3,5-Tris(trimethylsiloxymethyl)isocyanurate (XIXa) does not react with Me_3SiCl even at 100 °C.

The reactivity of the compounds under investigation with respect to Me_3SiCl decreases in the following series:

$$Me_2NCH_2OSiMe_3 \simeq Et_2NCH_2OSiMe_3 > MeC(O)NHCH_2OSiMe_3 >$$
$$> Me_2NC(O)NMeCH_2OSiMe_3 \simeq Et_2NC(O)NMeCH_2OSiMe_3 >$$
$$> [-N(CH_2OSiMe_3)C(O)]_3$$

2.4. Reactions with Trimethylacyloxysilanes

Dialkyl(trimethylsiloxymethyl)amines readily yield hexamethyldisiloxane also during condensation with trimethylacyloxysilane [11]:

$$R_2NCH_2OSiMe_3 + R'COOSiMe_3 \rightarrow R_2NCH_2OOCR' + (Me_3Si)_2O \quad (21)$$
$$R = Me, Et; \quad R' = Me, Ph, F_3C, CH_2{=}CH(CH_2)_8$$

In contrast to the condensation of trimethylalkoxysilanes with trimethylacyloxysilanes, this reaction proceeds under mild conditions and without a catalyst.

2.5. Reactions with Organylisocyanates

Unlike most organosilicon compounds containing C—O—Si system, N-(trimethylsiloxymethyl)amines, -azoles, and -amides react with organylisocyanates when heated or even in the cold (especially in the presence of 0.1% tin octoate). Such reactions yield trimethylsilyl esters of N,N-disubstituted carbamic acids (XXVII).

[13, 14]:

$$R-N=C=O + R'R''NCH_2OSiMe_3 \rightarrow \underset{XXVII}{R(R'R''NCH_2)NCOOSiMe_3} \quad (22)$$
$$\text{II}$$

R = R′ = R″ = Me (a); R = Me, R′ = R″ = Et (b);
R = Me, R′ = R″ = $CH_2=CH-CH_2$ (c); R = $CH_2=CH-CH_2$,
R′ = R″ = Me (d); R = $CH_2=CH-CH_2$, R′ = R″ = Et (e);
R = Ph, R′ = R″ = Me (f); R = Ph, R′ = R″ = Et (g);
R = Ph, R′R″ = C(Me)=CH—C(Me)=N (h); R = Ph,
R′ = $(CH_3)_2CH$, R″ = MeC(O) (i)

Thus, the insertion of isocyanate is accompanied by cleavage of the C—O bond in a molecule of II.

The structure of adducts XXVII has been confirmed by ^1H, ^{29}Si NMR, IR spectroscopy, and mass spectrometry. Heating of XXVII to 150-200 °C results in elimination of CO_2 and formation of 1,3,5-trialkylhexahydro-1,3,5-triazines (XXVIII) rather than RNCO isolation:

$$\underset{XXVII}{R(R'R''NCH_2)NCOOSiMe_3} \xrightarrow[-CO_2]{\Delta} [RN(CH_2NR'R'')SiMe_3] \rightarrow$$

$$\xrightarrow[-Me_3SiNR'R'']{} [RN=CH_2] \rightarrow 1/3 \quad \underset{XXVIII}{\text{(R-N, N-R)}} \quad (23)$$

This reaction is slow and proceeds even when XXVII is in storage. Yet most of these compounds may be distilled in a vacuum without decomposition.

Hydrolysis of the adducts XXVII at 20 °C or their boiling with absolute alcohol does not result in desilylation to the corresponding carbamates XXIX but proceeds as follows:

$$\underset{XXVII}{R(R'R''NCH_2)NCOOSiMe_3} \xrightarrow[-Me_3SiOH]{+HOH} \underset{XXIX}{[R(R'R''NCH_2)NCOOH]} \rightarrow$$

$$\xrightarrow[-CO_2]{} [RHNCH_2NR'R''] \xrightarrow[-R'R''NH]{} [RN=CH_2] \rightarrow 1/3 \quad \underset{XXVIII}{\text{(R-N, N-R)}} \quad (24)$$

As one goes from aromatic isocyanates to aliphatic ones, their reactivity with respect to II decreases drastically. N-(Trimethylsiloxymethyl)azoles and -amides react with RNCO at a slower rate, as compared to diorganyl(trimethylsiloxymethyl)amines.

Triorganylisocyanatosilanes, such as Me_3SiNCO, do not react with II.

Reaction (22) is sometimes accompanied by trimerization of organylisocyanates. For example, when IIa reacts with MeNCO, 6% of the latter convert into 1,3,5-trimethylisocyanurate. The main product, carbamate XXVIIa, has also been obtained in a counterreaction as follows:

$$Me(Me_3Si)NCOOSiMe_3 + Me_3SiOCH_2NMe_2 \xrightarrow[-(Me_3Si)_2O]{120-130\ ^\circ C} \rightarrow MeN(CH_2NMe_2)COOSiMe_3 \quad (25)$$

XXVIIa (92%)

2.6. Reactions with Ketene

Dialkyl(trimethylsiloxymethyl)amines react with ketene at 10-20 °C to yield hexamethyldisiloxane (97%) as follows:

$$\underset{II}{R_2NCH_2OSiMe_3} + CH_2=C=O \rightarrow \underset{XXX}{[R_2NCH_2CH_2COOSiMe_3]} \xrightarrow{+II} \rightarrow R_2NCH_2CH_2COOCH_2NR_2 + (Me_3Si)_2O \quad (26)$$

XXXI

R = Me, Et

Attempts to isolate intermediate trimethylsilyl esters of β-dialkylaminopropionic acid (XXX) have not been successful since the latter react with the starting II even at —60 to —70 °C to yield XXXI.

2.7. Reactions with Chloroanhydrides and Anhydrides of Carboxylic Acids

Dimethyl(trimethylsiloxymethyl)amine IIa dehydrochlorinates chloroanhydrides of alkanecarboxylic acids. The resulting ketenes undergo cyclodimerization (XXXII), and the hydrogen chloride that is eliminated breaks down IIa into dimethyl(chloromethyl)-amine and hexamethyldisiloxane:

$$\underset{IIa}{Me_2NCH_2OSiMe_3} + CH_3CH_2COCl \rightarrow \rightarrow CH_3CH=C(-O)-CH_3CH-C=O + [Me_2\overset{+}{N}=CH_2]Cl^- + (Me_3Si)_2O \quad (27)$$

XXXII

Conversely, benzoyl chloride yields trimethyl(benzoyloxy)silane (XXXIII) in the following reaction:

$$\underset{\text{IIa}}{Me_3SiOCH_2NMe_2} + PhCOCl \rightarrow \underset{\text{XXXIII}}{PhCOOSiMe_3} + [Me_2\overset{+}{N}=CH_2]Cl^- \qquad (28)$$

Anhydrides of carboxylic acids readily react with trimethylsilyl ethers of methylolamines. For example, when acetic anhydride reacts with dimethyl(trimethylsiloxymethyl)amine (IIa) in a molar ratio of 1:1, high yields of trimethylacetoxysilane and dimethyl-(aminomethyl)acetate (XXXIV) are obtained:

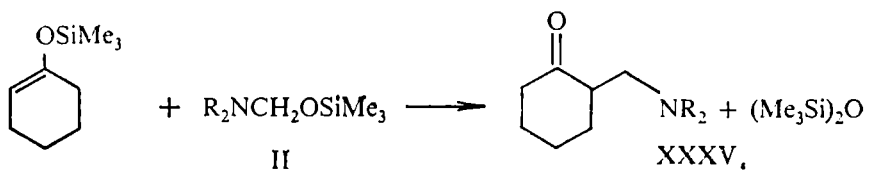
$$(MeCO)_2O + Me_2NCH_2OSiMe_3 \rightarrow \underset{\text{XXXIV}}{MeCOOCH_2NMe_2} + MeCOOSiMe_3 \qquad (29)$$

When IIa is taken in an excess amount, the latter compound is condensed with the resulting trimethylacetoxysilane so that hexamethyldisiloxane splits off:

$$Me_3SiOCH_2NMe_2 + MeCOOSiMe_3 \rightarrow Me_2NCH_2OOCMe + (Me_3Si)_2O \qquad (30)$$

2.8. Reactions with Trimethylsilyl Enol Ethers

Trimethylsilyl ethers of methylolamines react exothermally with the O-silylated enolates of ketones in acetonitrile in the presence of Me_3SiI (5 mol. %). The reactions result in high yields of the corresponding α-aminomethylated ketones (XXXV) plus hexamethyldisiloxane:



(31)

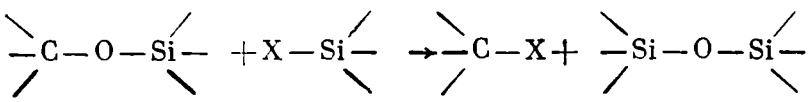
$R_2 = Me_2$ (a); $R_2 = Et_2$ (b); $R_2 = HC(O)Ph$ (c).

During short heating (1 hour) of 1-trimethylsiloxycyclohexene and N-(trimethylsiloxymethyl)benzamide quantitative α-amidomethylation takes place [15]. The mechanism of this reaction seems to include the step of intermediate formation of dialkyl(iodomethyl)amine: $[R_2\overset{+}{N}=CH_2]I^-$.

Reaction (31) suggests that II may act as effective C-aminomethylating reagents.

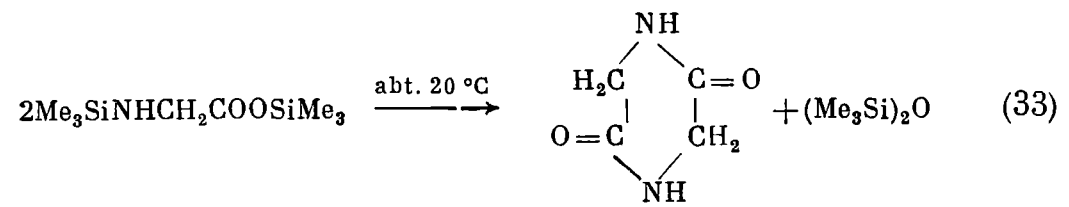
2.9. Dedisiloxanation Reactions

The previously discussed reactions of the trimethylsilyl ethers of methylolamines and methylolamides with chloro-, amino-, and acyloxytrimethylsilanes (see Secs. 2.2 through 2.4) are characterized by an extremely facile cleavage of the C—O—Si system and elimination of hexamethyldisiloxane. In the case of trimethylalkoxysilanes, this process most often occurs under more rigid conditions. In particular, the virtually quantitative elimination of hexamethyldisiloxane involves reaction between trimethylacyloxysilanes and trimethyl(dialkylamino)silanes as well as heating of the N,O-bis-trimethylsilyl derivatives of aminocarboxylic [16] and carbamic [17] acids to 100-200 °C. On the other hand, the N,O-bis-trimethylsilyl derivatives of amino alcohols and amino phenols do not detach hexamethyldisiloxane even at 200 °C. A comparison of these findings with the numerous published examples of the cleavage of the C—O—Si system with formation of hexamethyldisiloxane [18] suggests that the reaction of hexamethyldisiloxane detachment ("dedisiloxanation" reaction) is common in organosilicon chemistry. The ease with which it proceeds increases with polarization of the C—O—Si bonds:

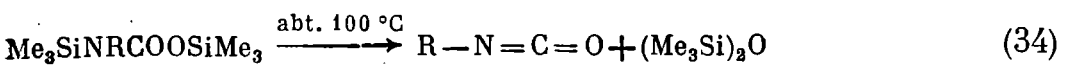


(32)

Elimination of hexamethyldisiloxane also becomes easier when it is possible to form a thermodynamically favourable cyclic structure* or when β-decomposition occurs:



(33)



(34)

The pronounced tendency of the trimethylsilyl ethers of methylolamines and methylolamides to enter into dedisiloxanation reaction [11] seems to be due to the geminal conjugation of the oxygen and nitrogen atoms. This results in ionization of the C—O bond as a consequence of the resonance structure of $R_2\overset{+}{N} = CH_2\overset{-}{O}SiMe_3$ being superimposed. The specific reactivity of N-(trimethylsiloxymethyl)-

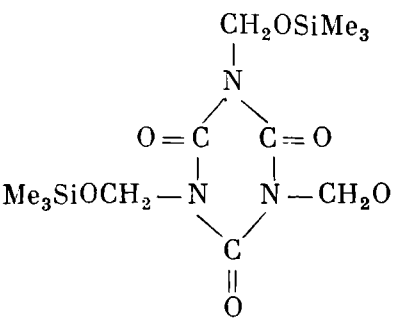
* Unlike N,O-bis-trimethylsilyl derivatives of aromatic amino acids stable up to 100 °C, N,O-bis-trimethylsilylglycine slowly detaches $(Me_3Si)_2O$ already at 20 °C.

amines and -amides allows one to classify them as effective amino- and amidoalkylating synthones. However, the synthetic capacity of these compounds as well as the dedisiloxanation reactions involving them seem to be broader in scope. These methods of synthesis open up radically new possibilities for conducting the "anhydrous" modification of the Mannich reaction in milder conditions, or amino-(amido)-alkylation in a neutral medium.

2.10. β-Elimination Reactions

The thermal stability of trimethylsilyl ethers of methylolamines, -azoles, and -amides increases according to the order in which they are mentioned here. A common property of these compounds, with few exceptions, is the reverse elimination of formaldehyde (β-decomposition) during heating. Depending on structure, the temperature of their decomposition varies widely:

$$Me_2NCH_2OSiMe_3 \underset{<100\ ^\circ C}{\overset{>125-130\ ^\circ C}{\rightleftharpoons}} Me_2NSiMe_3 + CH_2O \qquad (35)$$



$$Me_3SiOCH_2-\text{(N-azole)}-CH_2OSiMe_3 \underset{<150\ ^\circ C}{\overset{>250\ ^\circ C}{\rightleftharpoons}} 3Me_3SiNCO + 3CH_2O \qquad (36)$$

Reactions (35) and (36) are the first examples of β-decomposition in the $\equiv Si-O-CH_2-N\langle$ system.

Thermolysis of trimethyl(chloromethoxy)silane proceeds similarly to elimination of formaldehyde [19]. Trimethylsilylcarbonates containing a Si—O—C(O)—OR (R = Alk, Ar, or $SiMe_3$) system also show strong tendency for β-decomposition with the detachment of CO_2 [20]. A marked tendency for facile β-decomposition is also displayed by compounds containing a Si—N—C (O)—OR or Si—N = C—OR system [21].

These O-trimethylsilylurethanes (XXVII) were the first to display an extraordinary facility for β-elimination in the $\equiv Si-O-C(O)-N\langle$ fragment. For instance, unlike $Et_2NC(O)OSiMe_3$ which is stable at the boiling point (187 °C), compounds XXVII spontane-

ously eliminate CO_2 already at room temperature according to scheme (23).

Thus, just as the Si—C—C—X (where X is an electronegative substituent) system in β-carbofunctional organosilicon compounds [22], the silicon and X substituent in the Si—Y—C—X (Y = N, O) fragment also interact readily (β-effect). In chemical transformations, this manifests itself in a predominance of the β-elimination reaction which proceeds in the following manner:

$$Si-Y-C-X \rightarrow Si-X+Y=C \qquad (37)$$

This decomposition is possible only if there is no N—H bond. Otherwise, detachment of the HX molecule is most likely:

$$SiNH-CX \rightarrow SiN=C+HX \qquad (38)$$

As can be inferred from equation (38), we are dealing with the thermal decomposition of trimethylsilyl derivatives of urethanes and ureas, which have unsubstituted H atoms at N [23]. The products of reactions (4) and (5) of formaldehyde with organyl(trimethylsilyl)-amines and hexamethyldisilazane [7] also correspond to this scheme.

β-Decomposition in the Si—N—C—X system is more facile than in the Si—O—C—X fragment. This is indicated by the products yielded in thermolysis of N,O-bis(trimethylsilyl)urethanes [24]:

$$Me_3SiNRCOOSiMe_3 \xrightarrow{\Delta} RN=C=O+Me_3SiOSiMe_3 \qquad (39)$$

If an extrinsic compound affects the β-elimination reaction, then reaction can be explained by transfer of the reaction centre along the chain of the σ,σ- (or σ,π)-conjugation [25]. Thermal "spontaneous" β-elimination seems to be promoted by the intramolecular coordination of the silicon atom (which has vacant *d*-orbitals) with the donor X atom. The existence (or emergence in the transition state) of intramolecular coordination of the Si ← X bond is to some extent equivalent to a nucleophilic attack on the Si atom. As a result, a closed cycle is formed, and the chain of the σ,σ-conjugation becomes "involved" just as in the case of an ordinary nucleophilic attack by an extrinsic reagent:

(40)

In cases where the intramoleçular coordination is hindered, the same effect can be achieved intramolecularly. This occurs, for example, during β-decomposition of trialkylsilyl derivatives of benzoxazolone [26].

The foregoing suggests that a single approach can be taken to explain the anomalous properties of β-functional organosilicon compounds, and to predict the reactivity of other similar silicon compounds.

The insertion of a formaldehyde molecule into the Si—N bond is most likely to proceed through a similar four-centered coordination transition state.

It may be assumed that the interaction of other carbonyl-containing compounds with a Si—N bond proceeds in a similar manner:

(41)

$X = H_2,\ Cl_2; =O, =NR, =CH_2$

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10 Oligomerization Reactions of Substituted Vinylsilanes

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1. INTRODUCTION

The oligomerization reactions of Si-substituted vinylsilanes, $CH_2=CHSiX_3$ (I), and their cooligomerization with unsaturated hydrocarbons have come under the scrutiny of science only in fairly recent years following a comprehensive study of the oligomerization of olefins and dienes. The high activity of these unsaturated hydrocarbons has made it possible to produce higher unsaturated hydrocarbons with a predetermined structure by choosing the appropriate catalytic system and reaction conditions [1, 2]. The behaviour of I in oligomerization reactions resembles, to a certain extent, that of α-olefins. Yet, a complete analogy cannot be drawn between them. Silicon in I possesses less electronegativity and a larger atomic radius than the carbon, and vacant 3*d*-orbitals. Its presence alters the polarity of the double bond, and affects the course of oligomerization processes.

Comparison of the ^{13}C NMR spectra of I and their carbon analogues, $CH_2=CHCX_3$, II (Table 1) indicates that substitution of silicon for carbon in the $-CX_3$ group enhances the shielding of the α-carbon and deshields the β-carbon of the vinyl group [3-5].

Table 1. Chemical shifts in the ^{13}C NMR spectra (δ) and the spin-spin coupling constants (*J*) for vinylsilanes and their hydrocarbon analogues

Nos	Compound	δC_α, ppm	δC_β, ppm	$J_{C_\alpha-H}$, Hz	$J_{C_\beta-H}$, Hz
1	$CH_2=CHSi(CH_3)_3$	139.5	130.6	149	157
2	$CH_2=CHC(CH_3)_3$	149.0	109.0		
3	$CH_2=CHSiCl_3$	131.0	138.7	152	163
4	$CH_2=CHCCl_3$	141.2	115.2	173	161
5	$CH_2=CHSi(OCH_3)_3$	127.7	135.6	142	157
6	$CH_2=CHC(OCH_3)_3$	140.9	113.0		

In every case the signals of the carbon (C_α) attached directly to the silicon exhibit an upfield shift of 9 to 13 ppm, while the C_β signals are shifted downfield 21 to 23 ppm, as compared with II.

Substituent X has a roughly similar magnitude and direction of the inductive effect. This effect is exerted through the central carbon or the silicon on the carbon atoms of the vinyl group. Thus, the observable drop in the electron density of the double bond in I, against the isostructural II, can be rationalized by the occurrence of the

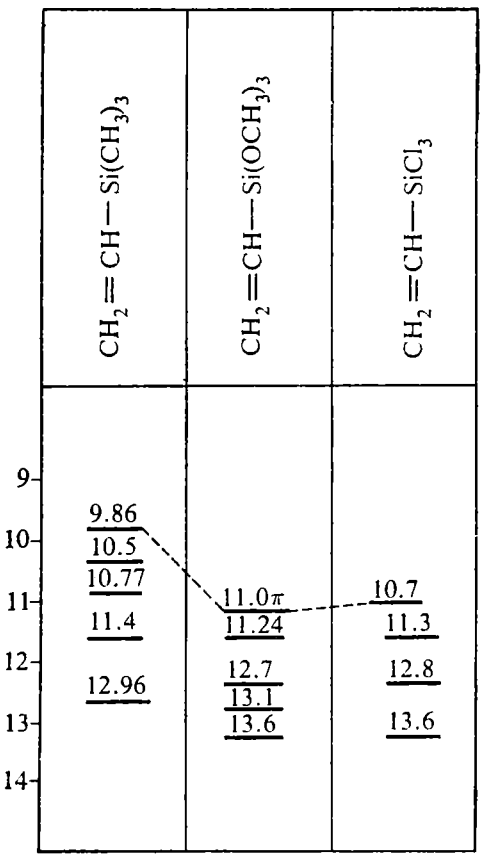


Figure 1. Energy levels of occupied molecular orbitals in substituted vinylsilanes

effect of the d_π-p_π interaction between the silicon and the vinyl group. The result is that part of the π-charge of the double bond is pulled off to the *d*-orbitals of the silicon.

The negative inductive effect of the substituents X and the effect of the d_π-p_π between the *d*-orbitals of the silicon and π-electrons of the double bond in these molecules act in the same direction enhancing the electron density at C_α. By contrast, in a molecule of trimethylvinylsilane (I, X = CH_3), the positive inductive effect produced by electron-donor methyl groups is only partially offset by the opposite effect of the d_π-p_π interaction and as a result the β-carbon of the vinyl group is shielded only poorly [6, 8].

The positions of the energy levels of the occupied molecular orbitals obtained from photoelectron spectra for I with X = CH_3, OCH_3, and Cl (Fig. 1) indicate that the substituents at the silicon, which reduce the electron density of the double bond, are arranged according to the order in which they are mentioned [4, 5]. The ionization potentials of the π-bond in I are in all cases greater than in the isostructural II. This can also be attributed to d_π-p_π interaction occurring in the molecules of I [9].

In all likelihood, the substituents X with σ-acceptor properties, facilitate the transfer of the p_π-electrons, by withdrawing electrons from the silicon atom, of the double bonds to the vacant *d*-orbitals of the silicon.

Table 2. Mass Spectra of Negative Ions for Dissociative Capture of Electrons by Molecules of Vinylsilanes, CH_2=CH—SiX_3 (relative intensities of mass lines are given as percentage of maximum intensity; the electron energy needed to form ions, eV (accurate to ±0.1 eV), is enclosed in brackets)

Ion	CH_2=CHSi$(CH_3)_3$	CH_2=CHSi$(OCH_3)_3$	CH_2=CHSiCl_3
$(M-H)^-$	100 (8.8)	1.9 (8.0)	—
	7.5 (3.7)	1.5 (6.7)	
$(CH-SiX_3)^-$	18.8 (8.6)	1.75 (7.8)	45.5 (7.6)
$(M-X_3)^-$	6.4 (9.0)	100 (6.3)	—
	25.0 (5.9)		
SiX_3^-	5.6 (6.0)	12.5 (7.2)	72 (6.1)
		16.0 (6.3)	44.7 (4.1)
X^-	6.25 (7.2)	100 (6.3)	100 (6.6)
CH_2^-	18.8 (9.2)	75.8 (8.4)	—
CH^-	23.8 (9.2)	35.0 (3.3)	—
O^-	—	12.5 (8.9)	—

This effect is confirmed by mass-spectrometric analysis of negative ions during the dissociative capture of electrons by the molecules of I (Table 2). The mass spectra of I show the ions of the $(CH-SiX_3)^-$ structure, formed by the rupture of the double bond, which does not normally take place in the dissociative capture of electrons by alkenes [10, 11]. The greater stability of the ions $(CH-SiX_3)^- \leftrightarrow CH=SiX_3$ seems to be due to the withdrawing of the p_π-electrons to the vacant *d*-orbitals of the silicon atom. This is responible for dissociation of the molecular negative ions that causes the double bond to be broken:

$$\left[CH_2=CH-SiX_3\right]^- \longleftrightarrow \left[CH_2-CH=SiX_3\right]^- \longleftrightarrow \left[CH_2=CH=SiX_3\right]^-$$

This evidence indirectly proves that the *d*-orbitals of the silicon are involved in the formation of the CH=Si< bond [4, 5].

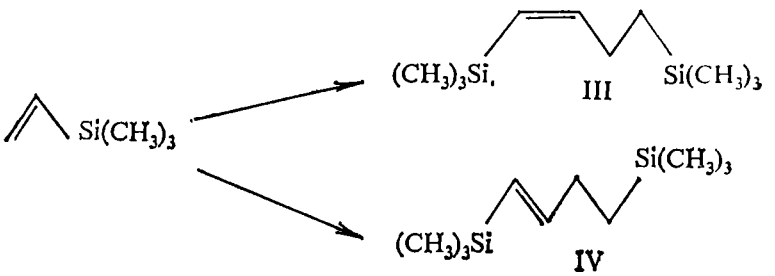
2. OLIGOMERIZATION OF Si-SUBSTITUTED VINYLSILANES (I)

The first data concerning the oligomerization of I yielding di-, tetra-, and octamers have been derived from studies into the polymerization of the monomers concerned [12, 13]. Controlled synthesis of the linear dimers of trimethyl- and triethylvinylsilane was performed in 1961 [14].

Extensive studies on the oligomerization of I, which were started in the 1970s, followed in-depth research into the oligomerization and cooligomerization reactions of olefins and dienes. A brief analysis of a few investigations conducted in this field will facilitate gaining insight into the behaviour of I in oligomerization processes. Complex organometallic systems have proved to be the most suitable catalysts for the oligomerization of lower olefins. They allow oligomers of predetermined structure to be synthesized selectively under mild conditions. Furthermore, catalysts that are formed in situ during the reaction between transition-metal compounds (nickel, cobalt, titanium, etc.) and organoaluminium compounds or Lewis acids hold the greatest promise for practical applications. Yields of α-olefin oligomers decrease in going from nickel to iron. Nickel complexes which are produced from the interaction of its salts with alkylaluminium halides have been found to be the most active. Under the influence of these catalysts, the dimers of ethylene and propylene are produced in yields greater than 90% at 20 °C and atmospheric pressure. In oligomerization, the activity of α-olefins decreases with increasing molecular weight. To illustrate, butene dimers have been obtained in yields lower than 70%. Under similar conditions, 1-pentene was found to give dimer in yields not greater than 40%, whereas 1-hexene virtually does not dimerize [1]. In addition to their high activity, complex organometallic catalysts with certain ligands allow the oligomerization of olefins to be channeled mainly towards the formation of specified oligomers. Specifically, the complex compounds of nickel with tertiary phosphines permit selective formation of 2,3-dimethylbutenes via the dimerization of propene [1].

Complex organometallic systems have also been found to catalyze the oligomerization reactions of I. With a catalyst that was prepared by treatment of cobalt 8-hydroxyquinolate with triethylaluminium in the presence of triphenylphosphine, trimethylvinylsilane dimerizes to form *cis*-1,4-bis(trimethylsilyl)butene-1 (III). At

100 °C and with a contact time of 10 hours, the yield of the dimer does not exceed 30%, while starting monomer is 45% converted. The reaction also gives *trans*-trimethylsilylbutene-2 in a yield of 3 to 5% as a result of the desilylation of dimer (III). Substitution of triphenylstibine for triphenylphosphine in the catalytic complex gives rise to *trans*-isomer (IV) in a 30% yield [15]:

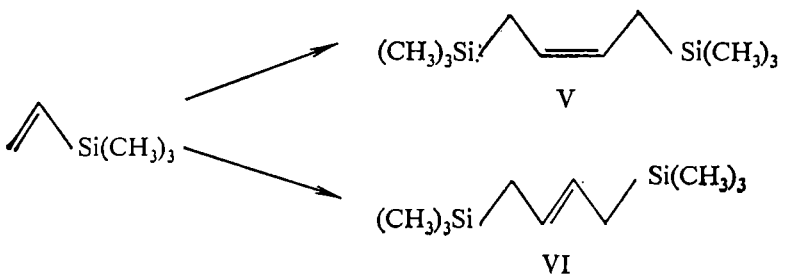


(1a)

(1b)

Thus, being highly effective in dimerizing butadiene, piperylene, and isoprene, the chelate compounds of cobalt are not very applicable to the synthesis of oligomers of I [16]. Attempts to enhance their catalytic activity using polar solvents, such as tetrahydrofuran and ether, have failed.

Higher activity has been shown by nickel-containing catalysts. In their presence the dimerization of trimethylvinylsilane proceeds to form a mixture of the geometric isomers of 1,4-bis(trimethylsilyl)-butene-2 (V), (VI):



(2a)

(2b)

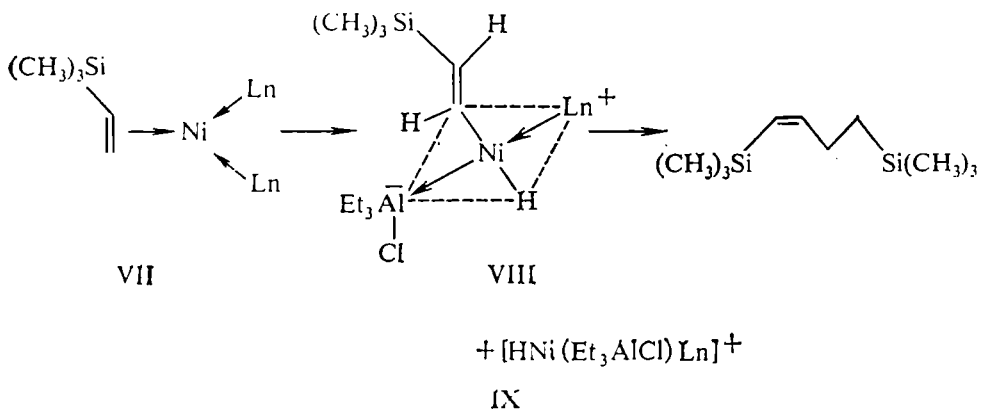
The activity of nickel catalysts is greatly influenced by the ligand environment of the central metal atom and by the conditions under which a catalytic complex is formed. Nickel acetylacetonate virtually does not catalyze the dimerization reaction of trimethylvinylsilane (the yield of the dimers does not exceed 20%, the polymer conversion is 32% [17]). Addition of trichlorosilane does not increase the yield even by introduction of an organophosphorus ligand. High yields (86%) of dimers V and VI and a 76% conversion of trimethylvinylsilane were obtained only with a catalytic system prepared by reduction of nickel acetylacetonate with triethylaluminium in the presence of triphenylphosphine (dichloroethylene used as solvent). Dimerization will not occur in the absence of solvent. Itis responsible for the formation of ethylaluminium chlorides from

the reaction between dichloroethylene and triethylaluminium (such reactions are catalyzed by nickel compounds):

$$ClCH=CHCl + AlEt_3 \begin{cases} \longrightarrow ClCH=CHEt + Et_2AlCl & (3a) \\ \longrightarrow ClCH=CHEt + EtAlCl_2 & (3b) \end{cases}$$

The fact that ethylaluminium chlorides participate in the oligomerization of trimethylvinylsilane is confirmed by using a catalyst prepared by the reduction of nickel chloride with aluminium ethylsesquichloride in the presence of triphenylphosphine. The yield of the dimer III is as high as 80%, and the conversion of the monomer is 71%.

Formation of the dimers (I) at nickel complexes may proceed as indicated below [5]:



(4)

VII VIII

+ [HNi (Et$_3$AlCl) Ln]$^+$

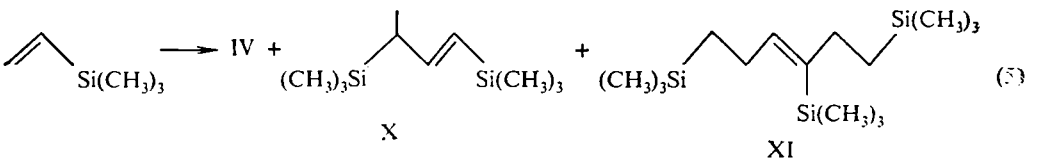
IX

The reaction of a chelate compound of nickel with an organoaluminium reducing agent yields a complex of zero-valent nickel (VII) with trimethylvinylsilane and ligands (Ln) coordinating around it. The complex of bivalent nickel (VIII) containing Ni—C and Ni—H bonds is stabilized due to the electron-donor effect of the ligand PPh_3 and the electron-acceptor properties of the Lewis acid Et_3AlCl. The complex VIII produces the Ni—C_β bond due to partial negative charge being concentrated across this carbon atom. A subsequent insertion of the second molecule of trimethylvinylsilane into the Ni—C bond creates a dimer product with the regeneration of the nickel-hydride complex IX.

It is well known that the Ziegler catalysts which incorporate titanium tetrachloride in combination with aluminiumalkyls find extensive application in the stereospecific polymerization of ethylene. Replacement of titanium tetrachloride by titanium alkoxides can bring about not only the polymerization but also the oligomerization of ethylene, giving di-, tri-, and tetramers. This reaction is affected by even minor changes in the composition of the catalyst.

The dimerization of propylene using these catalysts proceeds too slowly, they will never dimerize higher α-olefins.

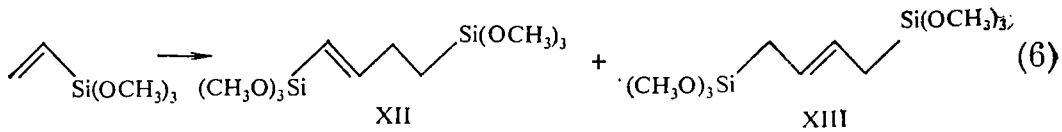
The compounds I are capable of undergoing oligomerization in the presence of titanium catalysts. In this reaction, the composition and yield of the reaction products are dependent on the species of the substituents at the silicon and the reaction conditions. Nickel and cobalt catalysts permit obtaining only unbranched dimers of trimethylvinylsilane, whereas the system $Ti(OC_4H_9)_4$-$AlEt_3$-PPh_3 promotes the formation of a linear dimer, as well as a branched dimer. In addition, this system produces a linear trimer, 1,3,6-tris-(trimethylsilyl)hexane-3, XI:



(5)

The ratio of the oligomers IV, X, and XI is 2:3:1. Their total yield is 50%, and the conversion of vinyltrimethylsilane, 50% [15]. The "titanium system" is the only system found to yield the trimer XI.

The activity of the catalytic system $Ti(OC_4H_9)_4$-$AlEt_3$-PPh_3 has also been found sufficient to dimerize I with X = OCH_3 and Cl, which are otherwise inert to the action of nickel and cobalt catalysts [5, 18]. The dimerization of vinyltrimethoxysilane proceeds with 1,4-bis(trimethoxysilyl)-*trans*-butene-1 (XII) formed as the predominant product. An isomeric dimer having double bond at 2-position (XIII) is formed only in modest amounts:

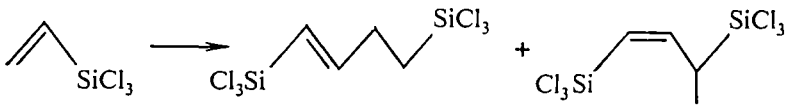


(6)

The total yields of dimers are as high as 73 to 80%, and the conversion of the monomer is 49 or 50%.

Under the effect of the "titanium system", vinyltrichlorosilane is dimerized less actively and gives a mixture of 1,4-bis(trichlorosilyl)-*trans*-butene-1 (XIV) and 1,3-bis(trichlorosilyl)-3-methyl-*cis*-propene-1 (XV) in 35% total yield. The monomer is 42% converted. The ratio of the reaction products, XIV and XV, depends on the duration of the process. A 6-hour process at 100 °C leads to a mixture with a 1 : 1 ratio of dimers XIV and XV. If the reaction lasts longer than 8 hours, the dimer XIV prevails in the reaction mixture with

the total yields of XIV and XV being unaffected:



XIV XV (7)

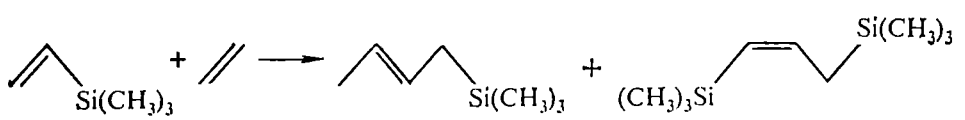
This evidence indicates that it is possible to oligomerize I using complex catalytic systems based on variable-valence metals. During this, trimethylvinylsilane, which contains electron-donor methyl groups at the silicon, which insignificantly increase electron density at the β-carbon, is oligomerized in the presence of catalytic systems containing Co, Ni, or Ti. By contrast, I with X = OCH_3 or Cl, where the α-carbon is shielded, is dimerized provided the "titanium system" is used.

3. COOLIGOMERIZATION OF VINYLSILANES WITH α-OLEFINS

Ethylene is known to enter into cooligomerization with propylene in the presence of alkylaluminium halides and nickel compounds [1]. Concurrently, homooligomerization of the starting monomers forms a complex mixture of butenes, pentenes, hexenes, and higher alkenes. Introduction of the electron-donor compounds of trivalent phosphorus into the catalytic system increases the conversion selectivity.

A higher conversion of starting monomers in combination with a predominant formation of the cooligomers C_5 has been observed when using catalysts containing bis(π-allylnickel bromide) or nickel oleate and excess aluminium ethylsesquichloride. Cooligomerization of ethylene with propylene using heterogeneous cobalt catalysts is effective although not adequately selective.

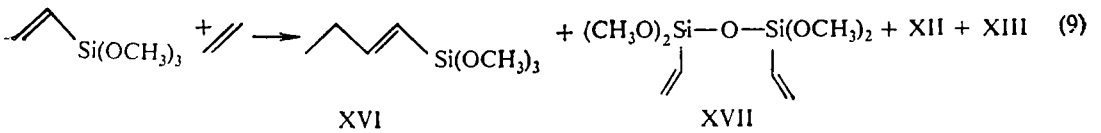
Complexes involving cobalt, nickel, and titanium yield cooligomers I with ethylene and propylene. The codimerization of trimethylvinylsilane with ethylene (in the molar ratio 1 : 1.5) in the presence of the cobalt 8-hydroxyquinolate-$AlEt_3$-PPh_3 at 120 °C, and 60 atm pressure, for 8 to 9 hours, yields a mixture of cooligomers, in a 1 : 1 ratio of the *cis*- and *trans*-isomers of trimethylsilylbutene-2, the total yield being 50%.



(8)

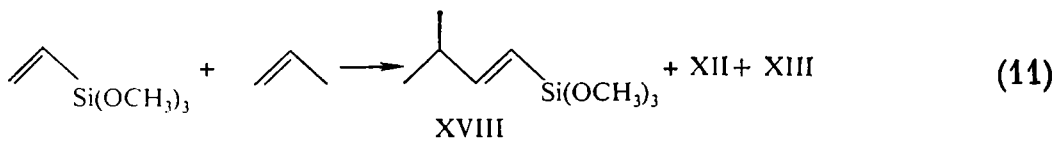
The homodimer of trimethylvinylsilane (III) has also been identified, and makes up 10% of the reaction products.

The cooligomerization of vinyltrimethoxysilane with ethylene proceeds in a more complicated fashion. In the presence of the $Ti(OBu)_4$-$AlEt_3$-PPh_3 system, trimethoxysilyl-*trans*-butene-1 (XVI) is produced in a 36% yield on the basis of the reacted monomer whose conversion is as high as 80% [5, 18, 19]. The linear homodimers of vinyltrimethoxysilane, XII and XIII as well as 1,3-divinyltetramethoxydisiloxane XVII are present in the reaction products:



The cooligomer of trimethylvinylsilane with propylene has been prepared by reacting the starting monomers in the presence of $NiCl_2$, ethylaluminiumsesquichloride, and PPh_3 at 120°C [5]. The linear dimers of trimethylvinylsilane, III and VI, have been found in the reaction products in 41% yield.

It has been possible to cooligomerize vinyltrimethoxysilane with a four-fold excess of propylene using a catalyst containing $Ti(OC_4H_9)_4$ [18, 19]. The yield of the codimer, i.e. trimethoxysilyl-3-methyl-*trans*-butene-1 (XVIII) does not exceed 28%, the monomer conversion being 31%. The formation of the dimerization products of vinyltrimethoxysilane, XII and XIII, has also been observed in this case.



The results of studies on the cooligomerization of I with α-olefins make it possible to note a number of regularities. The cooligomerization of trimethylvinylsilane with alkenes yields compounds where a double bond is in α,β- or β,γ-position with respect to the silicon atom. In the cooligomers of vinyltrimethoxysilane, the double bond is in the α,β-position to the silicon.

Despite the presence of excess α-olefins in the starting reaction mixture, their homooligomers are not formed. This is evidence that the coordination sphere of the metal initially incorporates a molecule of I. In a hydride complex of the catalyst, the proton is transferred to the α-carbon atom of trimethylvinylsilane. The ratio of the reaction products in which the percentage of homooligomers

of I is comparatively small suggests that the insertion rate of the α-olefin into the metal-carbon σ-bond is higher than that of the I molecule.

4. COOLIGOMERIZATION OF Si-SUBSTITUTED VINYLSILANES WITH POLYENES

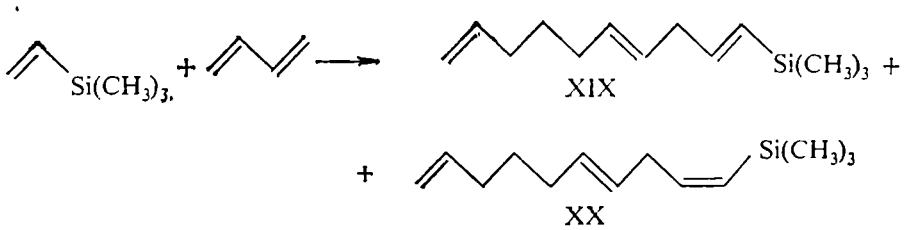
Complexes of cobalt, nickel, palladium, and titanium, which vary in their selectivity, are the most effective catalysts of cooligomerization reactions between α-olefins and dienes. The first three metals direct the cooligomerization of ethylene with butadiene primarily towards the formation of the geometric isomers of 1,4-hexadiene [2, 20, 21]. The complexes of titanium lead to 3-methylpentadiene-1,3 (94% selectivity) [22] or vinylcyclobutane with a lesser selectivity [23]. Under certain conditions, nickel catalysts promote the formation of cyclodecadiene-1,5, a cyclic cooligomer of butadiene with ethylene [23].

Propylene reacts with butadiene in the presence of nickel and cobalt complexes to give 2-methylhexadienes [2].

4-methylhexadiene-1,4 and 2,4-dimethylhexadiene-1,4, respectively, are the major products of the cooligomerization of isoprene with ethylene nd propylene [2].

Only one cooligomer, i.e. 3-methylhexadiene-1,4, is formed from piperylene and ethylene in the presence of nickel complexes [2]. As regards propylene, it reacts with piperylene to give a mixture of 2,3-dimethylhexadienes and substituted undecatrienes [24]. Thus, the products of the cooligomerization of α-olefins with dienes of varying structure can be prepared through choosing an adequate catalytic system and reaction conditions.

Nickel and titanium catalysts may be employed to cooligomerize I with dienes and trienes. In the presence of the system nickel acetylacetonate-$AlEt_3$-PPh_3, vinyltrimethylsilane reacts with butadiene-1,3 in the molar ratio 1 : 2 to afford an equivalent mixture of the *trans,trans*-(XIX), and *cis*-,*trans*-(XX) isomers of 1-trimethylsilyldecatriene-1,4,9 in 72% yield [25, 26]:

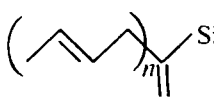


(12)

A change in the ratio of the starting reagents does not affect the composition of the reaction products. Under these conditions, homooligomers of monomers as well as cyclic oligomers will not be pro-

duced. Vinyltrimethoxysilane reacts with butadiene-1,3 to give nothing but 1-trimethoxysilyl-*cis*,*trans*-decatriene-1,4,9 in 85% yield based on the reacted $CH_2{=}CHSi(OCH_3)_3$ [25].

In the presence of the catalytic system $NiCl_2$-PPh_3-aluminium ethylsesquichloride, the reaction between butadiene and trimethylvinylsilane proceeds as a telomerization reaction path to give cooligomers with the general formula

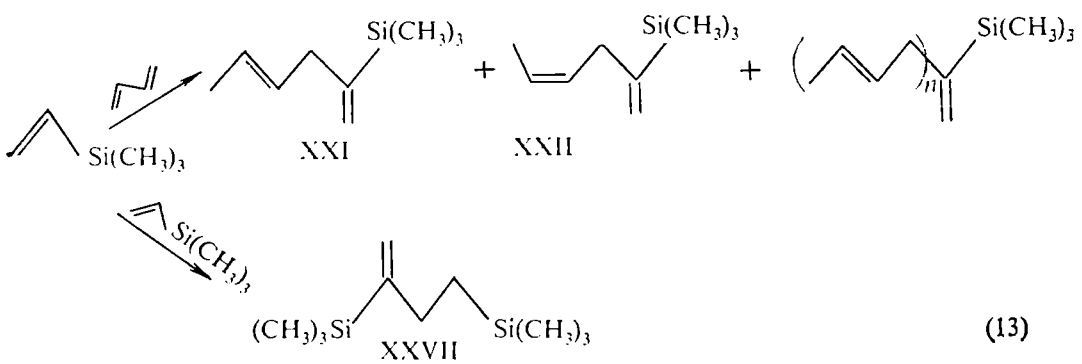


, where $n = 1-5$

The composition of the reaction products depends, to a large extent, on the conditions under which it is run. Heating of the initial reactants with a catalyst at 60 °C for 5 hours leads to a mixture of hexadienyl(C_6)- and decatrienlyl(C_{10})-trimethylsilanes in a 4:1 ratio with a 95% total yield, the amount of conversion of $CH_2{=}{=}CHSiMe_3$ being 42% [27]. The fraction C_6 consists of *trans*-XXI- and *cis*-XXII-isomers (3:1). 2-Trimethylsilyl-*trans*,*trans*-decatriene-1,4,8 (XXIII) is the principal component of the fraction C_{10}.

Apart from the C_6- and C_{10}-trimethylsilanes, tetradecatrienyl XXIV- and octadecapentaenyl XXV-trimethylsilanes (the ratio C_6: C_{10}:C_{18} = 3:1.5: 1:1) are formed in the reaction which runs for 8 hours at 100 °C. Here the overall yield of the oligomers drops as low as 73%, whereas the silane conversion rises as high as 85%. Some 9% of the mixture of the oligomers C_{22} (XXVI) were identified in the octadecapentaenyl fraction.

The formation of the 5-15% of the product of the dimerization of trimethylvinylsilane (XXVII) was observed in all cases. The yield of XXVII was found to increase to 30-40% with an increasing share of the trimethylvinylsilane in the initial mixture of the reactants.

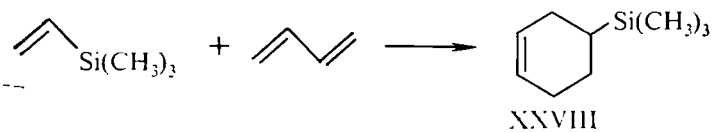


(13)

(XXIII, $n = 2$; XXIV, $n = 3$; XXV, $n = 4$, XXVI, $n = 5$)

Again, no formation of the homooligomers of butadiene-1,3 has been observed.

An attempt to employ palladium acetylacetonate to cooligomerize trimethylvinylsilane with butadiene-1,3 has yielded the product of diene synthesis, 3-(trimethylsilyl)cyclohexene (XXVIII) [17]:

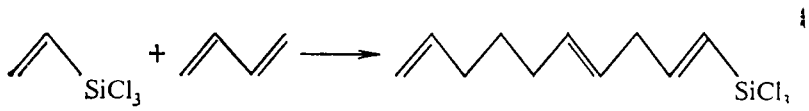


XXVIII [14]

In this case, the conversion of vinyltrimethylsilane has been found to approach 56%.

Vinyltrichlorosilane produces a similar cyclic adduct with butadiene in 60% yield, while the silane conversion is 69%.

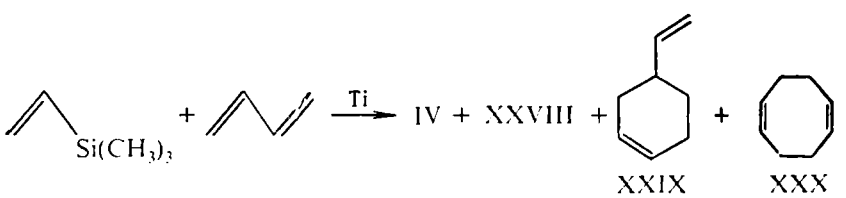
A linear cooligomer of vinyltrichlorosilane with butadiene-1,3 has been prepared in the molar ratio 1:2 in the presence of the catalytic system $Ti(OC_4H_9)_4$-$AlEt_3$-PPh_3 [18].



(15)

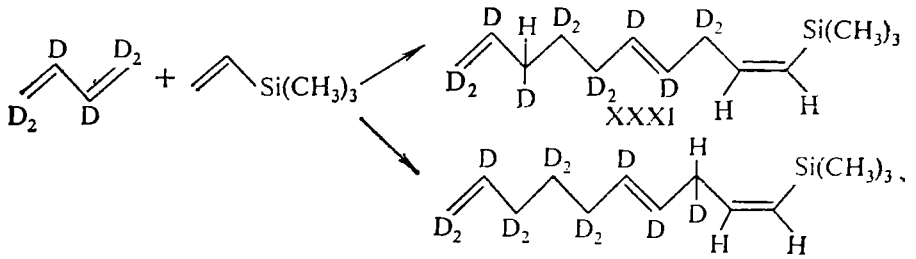
With the amount of conversion of vinyltrichlorosilane being 64%, the yield of the cooligomer increases to 40%. Higher non-distillable oligomers of unidentified composition are present in the reaction products.

The cooligomerization of trimethylvinylsilane with butadiene-1,3 in the presence of a "titanium catalyst" gives rise to a complex mixture containing up to 20% of the linear homodimer of trimethylvinylsilane (IV), a cyclic codimer (XXVIII), as well as the cyclodimerization products of butadiene, viz. vinylcyclohexene (XXIX) and 1,5-cyclooctadiene (XXX):



XXIX XXX (16)

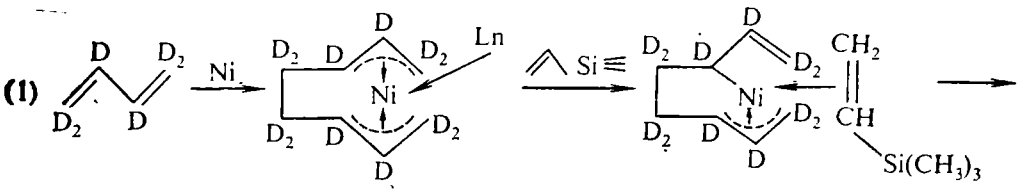
Study of the reaction between vinyltrimethylsilane and deuterated butadiene in the presence of nickel catalyst, which yields two deuterated isomers, XXXI and XXXII, suggests that the cooligomerization process proceeds as indicated below [25, 26]:



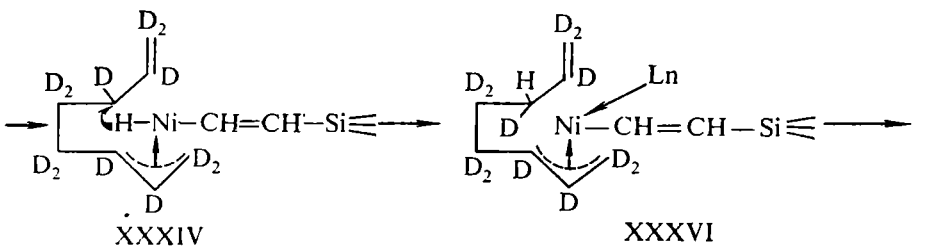
XXXI

XXXII

(17)

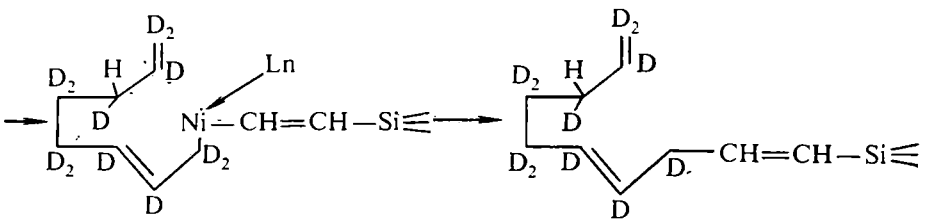


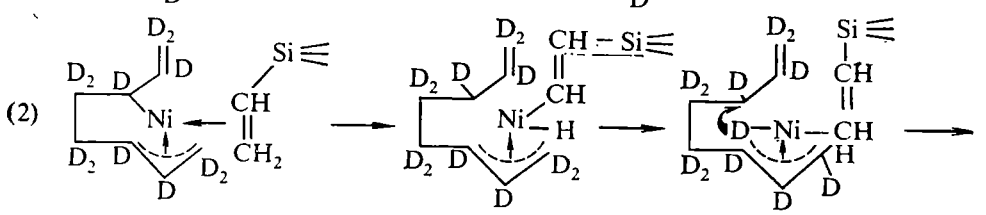
XXXIII



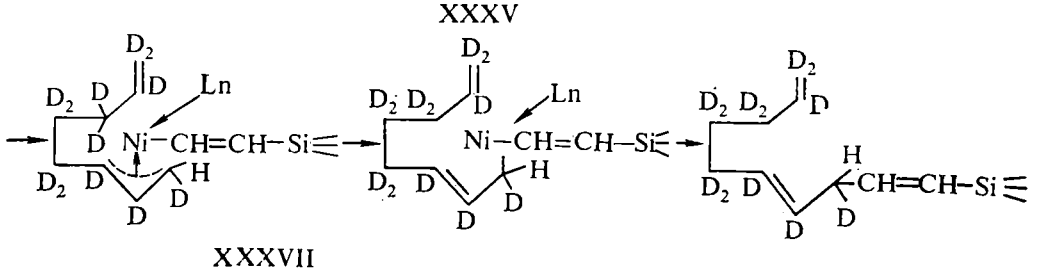
XXXIV

XXXVI





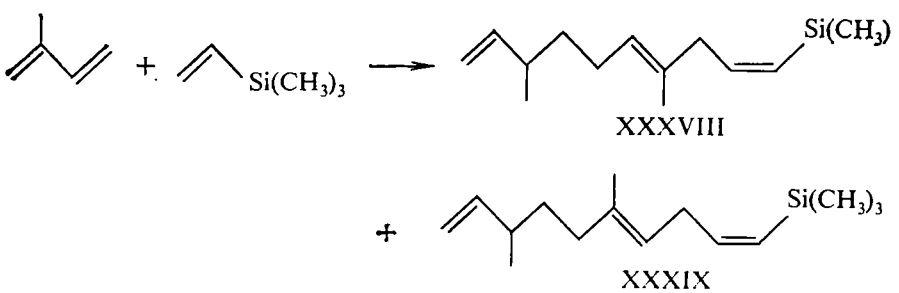
XXXV



XXXVII

At the initial step of the reaction, the coordination of two molecules of butadiene on the nickel atom produces a "wrench"-type π-complex, XXXIII. Oxidative addition of a molecule of vinyltrimethylsilane to the nickel atom leads to hydride complexes (XXXIV and XXXV) in which the proton is transferred to the activated butadiene molecule. The isomerization of the hydride complexes gives rise to σ-π-allyl complexes (XXXVI and XXXVII) and a subsequent formation of the C—Ni—C σ-bond. Replacement of the C—Ni—C bond by the C—C σ-bond is accomplished according to the route generally accepted for such reactions.

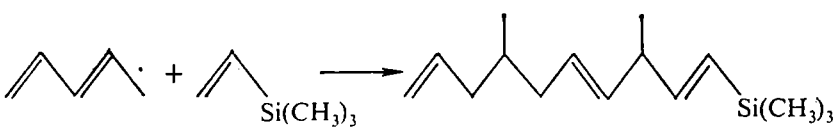
The cooligomerization of isoprene with trimethylvinylsilane has been carried out using nickel catalysts to give a mixture of the isomeric trimethylsilyl derivatives of trienes (XXXVIII and XXXIX) in the ratio 3:1, the total yield being 82% [25]:



(18)

Vinyltrimethoxysilane reacts with isoprene in a more selective fashion to produce individual 1-trimethoxysilyl-5,8-dimethyl-*cis*, *trans*-decatriene-1,4,9 in 75% yield.

1-trimethylsilyl-3,7-dimethyl-*trans*-decatriene-1,4,9 is the main product of the cooligomerization between trimethylvinylsilane and piperylene [28, 29]:

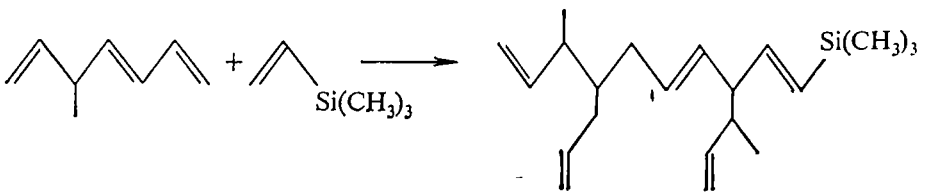


(19)

With the catalytic system $Ni(acac)_2$-$AlEt_3$-PPh_3, the reaction conducted at 100°C for 10 hours gives this cooligomer in 70% yield, the silane conversion being 50%.

Trimethylvinylsilane reacts less vigorously with 3-methylheptatriene-1,4,6. With a nickel-containing catalytic system, the *cis*- and *trans*-isomers of 1-trimethylsilyl-3-(1′-butene-3′-yl)-7-(1′-propene-3′-yl)-8-methyldecatriene-1,4,9 are formed in less than 30%.

yield [28]:



(20)

The cooligomerization of vinyltrimethylsilane with piperylene and 3-methylheptatriene-1,4,6 is accompanied by the formation of linear homooligomers in a yield no greater than 10%. A change in the molar ratio of the initial reagents does not affect the structure of the reaction products but does affect their yield.

The data cited suggest that I with X = CH_3, OCH_3, and Cl can add themselves to virtually any polyene. At the same time, an appropriate catalytic system and optimum conditions should be chosen for each specific case. A rough comparison of oligomerization involving I and α-olefins indicates that I are less reactive than ethylene and propylene but more reactive than higher α-olefins. The nature of the substituents X in the I molecule has a slight effect on the course of oligomerization reactions.

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11 Novel Vinyl-, Allyl-, and Cyclopropylsilane Derivatives

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Silicon-substituted olefins are extremely important in the study of silicon chemistry. They have theoretical importance as the subject of continuing research into the nature of the interaction of double bonded silicon. They have practical importance in the production of polymers with unique applied properties. We have refined the existing and designed new procedures for obtaining Si-substituted vinyl-, allyl-, and cyclopropylsilanes. We have then studied the properties of these species.

1. SYNTHESIS OF Si-SUBSTITUTED VINYL-, ALLYL-, AND CYCLOPROPYLSILANES

1.1. High-temperature Synthesis

Thermocondensation of hydrosilanes, $Cl_n(CH_3)_{3-n}SiH$ (I), with vinyl chloride or chlorobenzene in the gas phase at 500-550 °C in the presence of hydrocarbon halides ($HCClF_2$, CH_2Cl_2, CF_2Cl_2, and $CF_2{=}CF_2$) appreciably raises the yield of Si-substituted vinyl- or phenylsilanes (Table 1) [1-4]:

$$Cl_n(CH_3)_{3-n}SiH + ClCH{=}CH_2 \xrightarrow{500-550\,^\circ C} \rightarrow Cl_n(CH_3)_{3-n}SiCH{=}CH_2 + HCl \quad (1)$$

II

Table 1. Effect of $HCClF_2$ on the Yield of Vinylsilane Derivatives in High-temperature Condensation of $Cl_n(CH_3)_{3-n}SiH$ with Vinyl Chloride

Yield, %	$Cl_n(CH_3)_{3-n}Si(CH{=}CH_2)$			
	$n = 3$	$n = 2$	$n = 1$	$n = 0$
In the presence of $HCClF_2$	95	85	50	40
In the absence of $HCClF_2$	85	65	24	6

The corresponding derivatives of 2,2-difluorocyclopropylsilane (III) and 3,3-difluoroallylsilane (IV) have been identified in the reaction mixtures produced via condensation of $Cl_n(CH_3)_{3-n}SiH$ with vinyl chloride in the presence of $HCClF_2$ [5]. One could expect that the compounds referred to above are the product of the reaction between the yielded vinylsilane derivative and difluorocarbene generated from difluorochloromethane [6]:

$$Cl_n(CH_3)_{3-n}SiCH=CH_2 \xrightarrow{:CF_2} Cl_n(CH_3)_{3-n}SiCH(CF_2)-CH_2 \quad \text{III} \quad (2)$$

$$\downarrow$$

$$n=0\text{-}3 \qquad Cl_n(CH_3)_{3-n}SiCH_2CH=CF_2 \quad \text{IV}$$

To test this hypothesis, $Cl_n(CH_3)_{3-n}SiCH=CH_2$ was reacted with $HCClF_2$ to give compounds III and IV. Product III is also formed when reaction (2) involves other sources of difluorocarbene like trimethyl(trifluoroacetoxy)silane [7]. Application of tetrafluoroethylene instead of difluorochloromethane lowers the yield of III to 3%, a derivative of 2,2,3,3-tetrafluorocyclobutylsilane (V) being the major reaction product [7]:

$$Cl_n(CH_3)_{3-n}SiCH=CH_2+CF_2=CF_2 \xrightarrow{400\,^\circ C} Cl_n(CH_3)_{3-n}SiCH(CF_2-CF_2)-CH_2 \quad \text{V} \quad (3)$$

The activity of the double bond in olefins in the reaction between trimethylalkenylsilane and difluorocarbene generated from difluorochloromethane drops as its distance from the silicon increases (Table 2):

$$(CH_3)_3Si(CH_2)_nCH=CH_2+HCClF_2 \xrightarrow{500-530\,^\circ C} (CH_3)_3Si(CH_2)_nCH(CF_2)-CH_2+HCl \quad \text{VI} \quad (4)$$

$n=0\text{-}2$

Table 2. Yields of Products of Addition of Difluorocarbene (VI) and Tetrafluoroethylene (VII) to $(CH_3)_3Si(CH_2)_nCH=CH_2$

Compound	Yield, %		
	$n=0$	$n=1$	$n=2$
VI	19	7	2
VII	17	25	29

At the same time, the remoteness of the double bond from the silicon raises the yield of the product in the cycloaddition of tetrafluoroethylene to trimethylalkenylsilanes

$$(CH_3)_3Si(CH_2)_nCH=CH_2+CF_2=CF_2 \xrightarrow{400\ ^\circ C}$$

$$\rightarrow (CH_3)_3Si(CH_2)_nCH(CF_2)CH_2CF_2 \quad (5)$$

VII

The nature of substituents at the silicon also exerts a pronounced effect on the yield of the cycloaddition products when the derivatives of vinylsilane react with tetrafluoroethylene or difluorocarbene. For instance, an increase in the number of chlorine atoms, n, in the molecule of $Cl_n(CH_3)_{3-n}SiCH=CH_2$ diminishes the reactivity of the double hond.

Chlorine-substituted 2,2-difluorocyclopropane and 2,2,3,3-tetrafluorocyclobutane enter into thermal condensation with methyldichlorosilane as indicated below [1]:

$$Cl_2CH_3SiH+ClCH(CF_2)CH_2 \xrightarrow{510\ ^\circ C} CH_3Cl_2SiCH(CF_2)CH_2 \quad (6)$$

$$Cl_2CH_3SiH+ClCH(CF_2)CF_2CH_2 \xrightarrow{510\ ^\circ C} CH_3Cl_2SiCH(CF_2)CF_2CH_2 \quad (7)$$

This fact indicates the unsaturated nature of fluorosubstituted fluoropropyl and cyclobutyl groups, since aliphatic chlorides do not enter into the gas thermal condensation reaction.

The thermocondensation reaction of trichloro- and trimethylsilane with polychloroethylene at 500-650 °C leads to a mixture of the corresponding chlorovinylsilane derivatives, 1,2-bis-silylethylene and bis-silylacetylene, obtained in 10-70% yields [8]:

$$X_3SiH+ClCH=HCCl \xrightarrow[-HCl]{}$$

$$\rightarrow X_3SiCH=CHCl+X_3SiCH=CHSiX_3+X_3SiC\equiv CH \quad (8)$$

$$X_3SiH+Cl_2C=YCCl \xrightarrow[-HCl]{}$$

$$\rightarrow X_3SiCY=CCl_2+X_3SiCH=CHSiX_3+X_3SiC\equiv CSiX_3+X_3SiC\equiv CH \quad (9)$$

$X=Cl,\ CH_3;\quad Y=H,\ Cl$

1.2. Organomagnesium Synthesis

Vinyl chloride reacts with a mixture of magnesium and trimethylchlorosilane in THF to give trimethylvinylsilane (80-85% yield) [3, 9]:

$$(CH_3)_3SiCl + Mg + ClCH=CH_2 \xrightarrow{THF} (CH_3)_3SiCH=CH_2 + MgCl_2 \quad (10)$$

However, attempts at making $(CH_3)_{4-n}Si(CH=CH_2)_n$ from $(CH_3)_{4-n}SiCl_n$ (n = 2-4) in a similar fashion have failed [11]. In contrast, reaction of the latter with the vinylmagnesium chloride prepared beforehand has yielded the expected products of vinylation [11]:

$$(CH_3)_{4-n}SiCl_n + nClMgCH=CH_2 \xrightarrow{THF} (CH_3)_{4-n}Si(CH=CH_2)_n \quad (11)$$
$$n = 1\text{-}4$$

Utilization of a THF-inert solvent mixture significantly decreases the yields of complete vinylation products [11].

The reactivity of the vinylchlorosilanes $(CH_2=CH)_{4-n}SiCl_n$ in reaction with vinyl- and methylmagnesium chloride drops with the n number varying in the order: $1 > 2 \geqslant 3$ [11, 12].

Thus, the availability of the vinyl group at the silicon bound to the 1-3 chlorine atoms enhances the Si—Cl bond activity in reactions involving organomagnesium reagents.

The reaction between vinyl chloride and magnesium and dimethyldichlorosilane in THF yields a mixture of tetramethyl(1,2-divinyl)-disilane (VIII) and hexamethyl(1,3-divinyl)trisilane (IX) [12]:

$$(CH_3)_2SiCl_2 + Mg + ClCH_2=CH_2 \xrightarrow[-MgCl_2]{} CH_2=CH(CH_3)_2SiCl \xrightarrow{+Mg} \rightarrow CH_2=CH(CH_3)_2SiMgCl + \xrightarrow[-MgCl_2]{CH_2=CH(CH_3)_2SiCl} [CH_2=CH(CH_3)_2Si]_2 \quad (12)$$
$$\text{VIII}$$

$$2CH_2=CH(CH_3)_2SiMgCl + (CH_3)_2SiCl_2 \rightarrow \rightarrow [CH_2=CH(CH_3)_2Si]_2Si(CH_3)_2 + 2MgCl_2 \quad (13)$$
$$\text{IX}$$

Compound VIII results from the action of methylmagnesium chloride on methylvinylchlorosilane in situ:

$$CH_3(CH_2=CH)SiCl_2 \xrightarrow[THF]{+2Mg+CH_3Cl} \rightarrow [(CH_3)_2(CH_2=CH)Si]_2 + (CH_3)_3SiCH=CH_2 \quad (14)$$

This fact indicates that dimethylvinylchlorosilane reacts with magnesium in THF to yield a silicon analogue of Grignard reagent,

which is then condensed with chlorosilane to give VIII. This has been corroborated experimentally [13]. Other workers obtained similar results later [14].

On the contrary, when reacting with Mg in THF, other compounds of the type $R(CH_3)_2SiCl$ (where R = H, CH_3, $CH_2{=}CH{=}CH_2$) produce no corresponding disilane derivatives. Yet under the same conditions, dimethylphenylchlorosilane is converted to tetramethyl(1,2-diphenyl)disilane in 20% yield. The reaction between $(CH_3)_2(CH_2{=}CH)SiCl$ and magnesium and triorganylchlorosilanes results in a mixture of corresponding disilane derivatives [10]:

$$3(CH_2{=}CH)(CH_3)_2SiCl + 2Mg + ClSi(CH_3)_2R \xrightarrow{THF} \rightarrow \text{VIII} + (CH_2{=}CH)(CH_3)_2Si{-}SiR(CH_3)_2 + 2MgCl_2 \quad (15)$$

R = H, Me, $CH_2{=}CHCH_2$, C_6H_5

These data are evidence that dimethylvinylchlorosilane reacts with magnesium in THF, producing a silicon analogue of the Grignard reagent.

Reactions involving vinylmagnesium chloride in situ and other methylorganyldichlorosilanes $R(CH_3)SiCl_2$ (R = H, $CH_2{=}CH$, $CH_2{=}CHCH_2$, C_6H_5) proceed according to the schemes that are similar to (12) and (13) [10].

Organosilicon magnesium compounds will be formed provided a vinyl or phenyl group is at the silicon. This can be explained by the stabilization of the intermediates, $RR'_2SiMgCl$ (R = $CH_2{=}CH$, C_6H_5), by σ,π-conjugation of the Si—Mg electron bond system and C=C bond.

This is also borne out by the fact that the formation of disilane derivatives is more facile, the greater the number of vinyl groups bound to the SiCl grouping.

1.3. Organometallic Synthesis of Organosilicon Derivatives of Cyclopropane

High-temperature reactions similar to those described in Sec. 1.1 are not applicable to the synthesis of the organosilicon derivatives of cyclopropane because of their low thermal stability. To obtain these compounds, the Simmons-Smith reaction has been modified [15] to use pelletized zinc instead of the powdered one.

$$R_n(CH_3)_{3-n}Si(CH_2)_mCH{=}CHR' + CH_2I_2 \xrightarrow[-ZnI_2]{Zn/Cu} R_n(CH_3)_{3-n}Si(CH_2)_m\nabla R' \quad (16)$$

$n = 0\text{-}3$; $m = 0\text{-}2$;

R = H, CH_3, CH_3O, C_2H_5O; F, Cl; R' = H, C_2H_5, C_4H_9, Cl, $OSi(CH_3)_3$

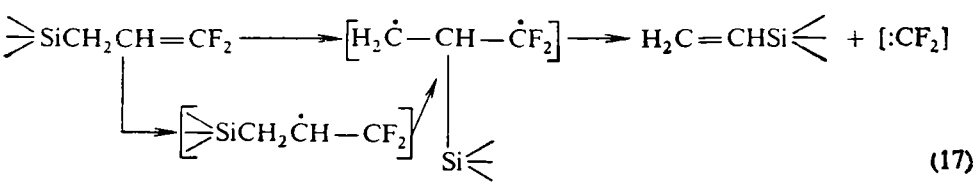
Vinyltrimethoxysilane and methylvinylethoxysilanes smoothly enter into reaction (16) giving respective adducts in 77-78% yields. This permits tetraethoxy- or tetramethoxysilanes to be utilized as solvents in the reaction referred to above [15]. Such solvents have made it possible to use other compounds, such as $R_3SiCH=CHCl$ ($R = CH_3$, CH_3O), in reaction (16) even though they are not normally used [4].

2. CHEMICAL AND PHYSICOCHEMICAL PROPERTIES OF Si-SUBSTITUTED VINYL-, ALLYL-, AND CYCLOPROPYLSILANES

A study has been made into some chemical properties of Si-substituted vinyl-, allyl-, and cyclopropylsilanes with a view to elucidating the nature of interaction of silicon when double bonded or in a three-membered cycle.

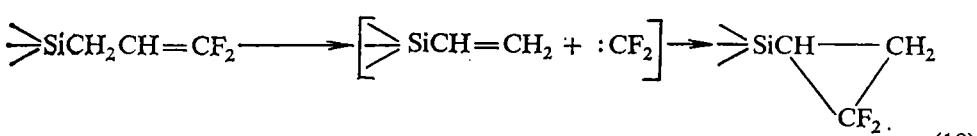
2.1. Thermal Conversions of Si-substituted Vinyl-, Allyl-, and Cyclopropylsilanes

During thermolysis of Si-substituted 3,3-difluoroallylsilane, 1,2-migration of the silyl group occurs and a corresponding derivative of vinylsilane is produced as shown schematically below [3, 4]:



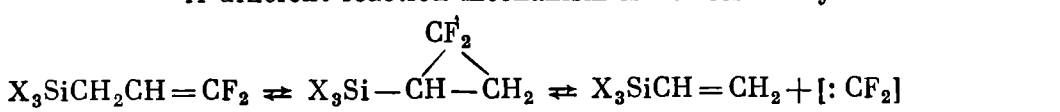
(17)

Reaction (17) does not yield a 2,2-difluorovinylsilane derivative (the elimination product of an α-methylene group [16]). The formation of difluorocarbene during thermolysis of the derivatives of 3,3-difluoroallylsilane is shown by the production of the corresponding substituted difluorocyclopropylsilane:*

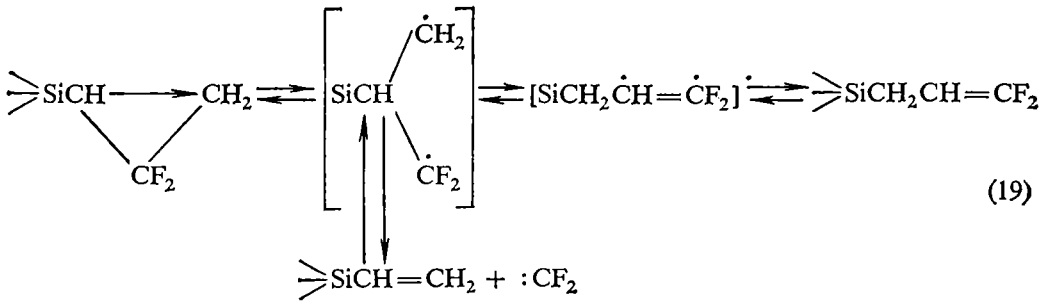


(18)

* A different reaction mechanism is no less likely:



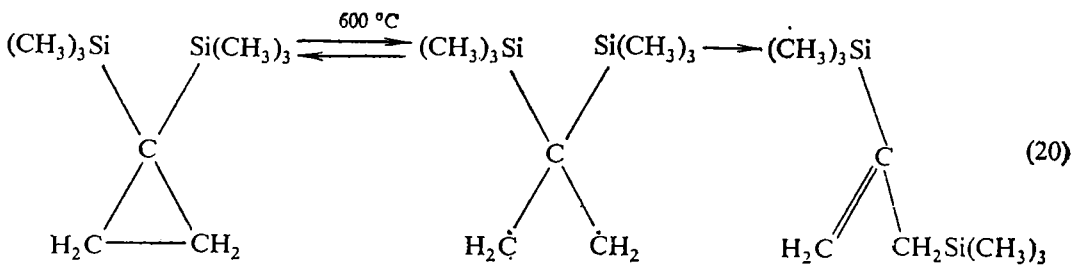
Therefore, thermolysis of the derivatives of 3,3-difluoroallyl- and 2,2-difluorocyclopropylsilane can be envisioned as a series of reversible processes which pass through a general biradical form of the transient state of the molecule [15, 17]:



(19)

The identical mass spectra of $\overline{CF_2CH_2\dot{C}HSi(CH_3)_{3-n}X_n}$ (X = H, F, Cl; n = 0-3) and $F_2C{=}CHCH_2Si(CH_3)X_2$ (X = H, F, Cl, CH_3) are evidence in favour of scheme (19) [18].

Thermolysis of 1,1-bis(trimethylsilyl)cyclopropane at 660 °C proceeds as indicated below:



(20)

The above scheme indicates a 1,2-migration of the trimethylsilyl group [3].

2.2. Reaction of Trimethyl- and Vinyltrichlorosilane with Chloroethylenes

Reaction of trimethyl- and vinyltrichlorosilane with chloroethylenes involves the breaking of the Si—C bond, elimination of vinyl chloride, and formation of a new Si—C bond:

$$X_3SiCH{=}CH_2 + Cl{-}R \xrightarrow{500-600\,^\circ C} X_3SiR + ClCH{-}CH_2 \qquad (21)$$

X = CH_3, Cl; R = CH = CHCl, CH = CCl_2, CCl = CCl_2, CH = $CHSiCl_3$

2-chlorovinyltrichlorosilane reacts with the chlorine derivatives of ethylene to yield ethyltrichlorosilane:

$$Cl_3SiCH{=}CHCl + ClCX{=}CXY \xrightarrow{500-600\,^\circ C} Cl_3SiC{\equiv}CH + HCl \qquad (22)$$

X, Y = H, Cl

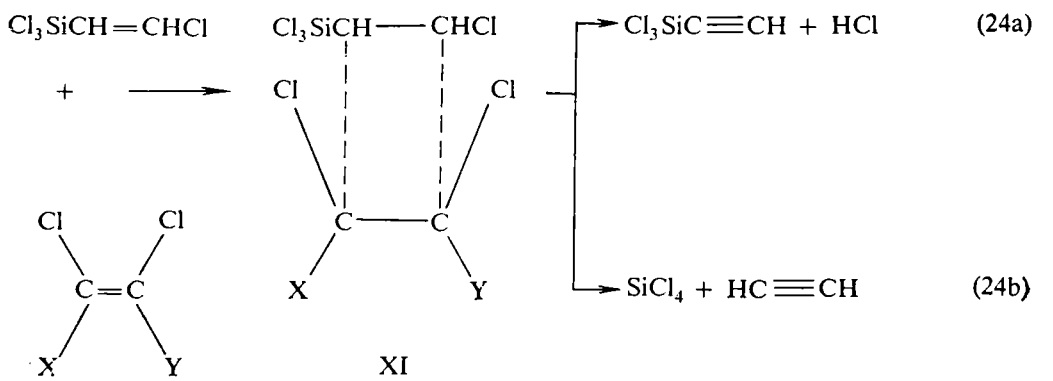
At the same time, during pyrolysis of individual 2-chlorovinyltrichlorosilane (as well as in the presence of CCl_4, $CHCl_3$, and CH_2Cl_2 as sources of radicals and carbenes), no sizable amounts of ethynyltrichlorosilane are formed. The high-temperature reaction of Si-hexachloro- or Si-hexamethyl-1,2-disilylethylene with mono-, di-, tri-, and tetrachloroethylene yields a mixture of corresponding Si-substituted chlorinated vinylsilanes, ethynylsilane, and disilylacetylene:

$$X_3SiCH=CHSiX_3 + Cl_mH_{2-m}C=CH_{2-n}Cl_n \rightarrow$$
$$\rightarrow X_3SiCl_{m-1}H_{2-m}C=CH_{2-n}Cl_n + X_3SiC\equiv CH + X_3SiC\equiv CSiX_3 \quad (23)$$
$X = Cl,\ CH_3;\ m = 1,\ 2;\ n = 0\text{-}2.$

The products of reactions (21) and (23) apparently result from a homolytic exchange of the radicals $CH_2=CH$ and R by analogy with reaction (19)

$$Cl_n(CH_3)_{3-n}SiCH=CH_2 + HSiCl_m(CH_3)_{3-m} \rightleftarrows$$
$$\rightleftarrows Cl_n(CH_3)_{3-n}SiH + CH_2=CHSiCl_m(CH_3)_{3-m}$$

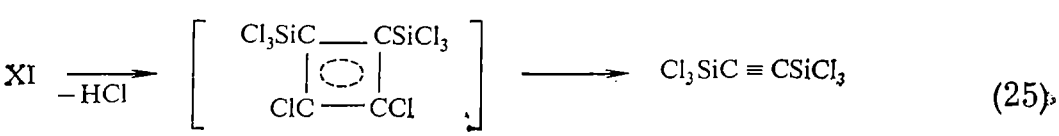
In the reaction involving dehydrochlorination of 2-chlorovinyltrichlorosilane, the chlorine derivatives of ethylene appear to be responsible for the intermediate formation of cyclic adducts that either dissociate into the starting or novel compounds or, as a consequence of β-elimination, decompose to give HCl and $SiCl_4$ [8]:



XI

X, Y = H, Cl

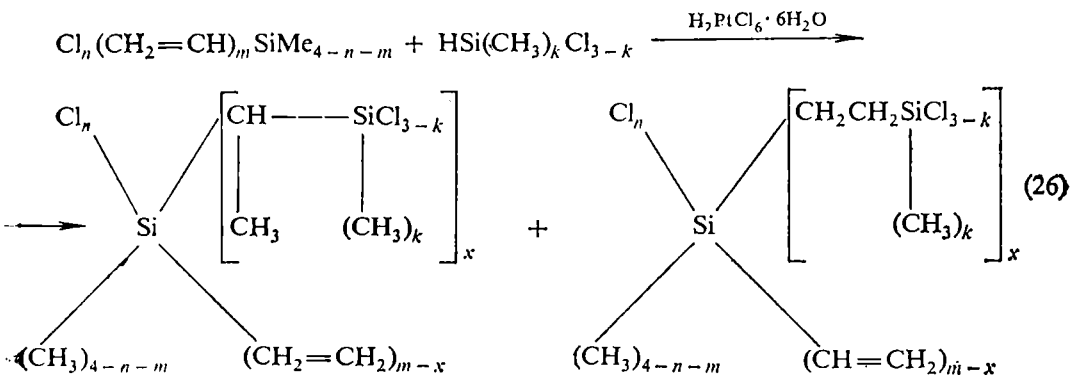
The formation of bis(trichlorosilyl)acetylene in reaction (23) can be explained in a similar fashion:



X = Y = Cl

2.3. Hydrosilylation of Si-substituted Vinylsilanes

Hydrosilylation of the derivatives of mono-, di-, and trivinylsilane as well as tetravinylsilane proceeds in a nonregioselective manner giving a mixture of α- and β-adducts, with the latter being predominant [20]:



(26)

α-adduct (XII) β-adduct (XIII)

$m, x = 1\text{-}4$; $n, k = 0\text{-}3$

The ratio of the species under review is dependent on the structure of both reactants (Table 3).

Hydrosilylation of trimethylvinylsilane almost solely yields the β-adduct. At the same time, when $HSiCl_3$ is added to vinyltrichlorosilane and CH_3SiCl_2H to tetravinylsilane, the α- and β-adducts are in the ratios of 1.0 : 1.5 and 1.0 : 1.2, respectively.

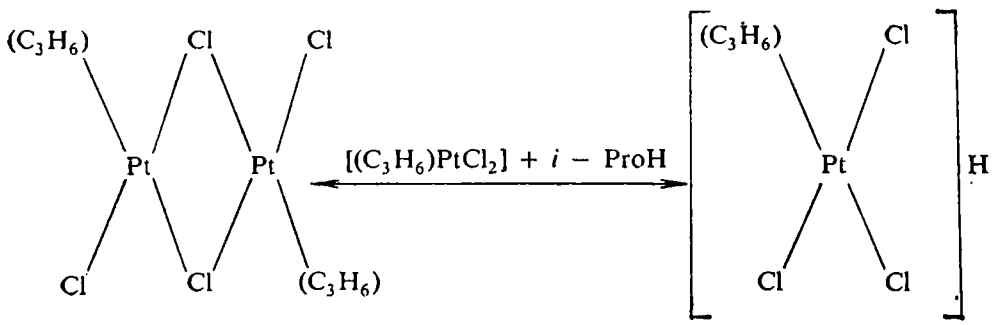
Table 3. The Ratio of the Isomeric Adducts, $(CH_3)_kSiHCl_{3-k}$ (XII) and $(CH_3)_{4-m-n}SiCl_n(CH_2{=}CH)_m$ (XIII)

	Ratio of α- to β-adducts			
	$(CH_3)_3SiH$	$Cl(CH_3)_2SiH$	$Cl_2(CH_3)SiH$	Cl_3SiH
$Si(CH{=}CH_2)_4$	20/80	25/75	45/55	10/90
$CH_3Si(CH{=}CH_2)_3$	12/88	5/95	20/80	35/65
$(CH_3)_2Si(CH{=}CH_2)_2$	24/76	6/94	13/87	18/82
$(CH_3)_3SiCH{=}CH_2$	10/90	5/95	5/95	3/97
$ClSi(CH{=}CH_2)_3$	28/72	15/85	17/83	0/100
$Cl_2Si(CH{=}CH_2)_2$	40/60	16/84	9/91	0/100
$Cl_3SiCH{=}CH_2$	25/75	10/90	20/80	40/60
$Cl(CH_3)Si(CH{=}CH_2)_2$	22/78	19/81	16/84	0/100
$Cl(CH_3)_2SiCH{=}CH_2$	18/82	8/92	7/93	4/96
$Cl_2(CH_3)SiCH{=}CH_2$	0/100	6/94	5/95	3/97

Hydrosilylation of trimethylvinylsilane by triphenyl-, methyldiphenyl-, and dimethylphenylsilane proceeds regiospecifically, the minimum ratio of the α- and β-adducts being 1 : 19. Addition of dimethylphenylsilane to vinyltrichlorosilane and tetravinylsilane reduces the above ratio to 1 : 3.

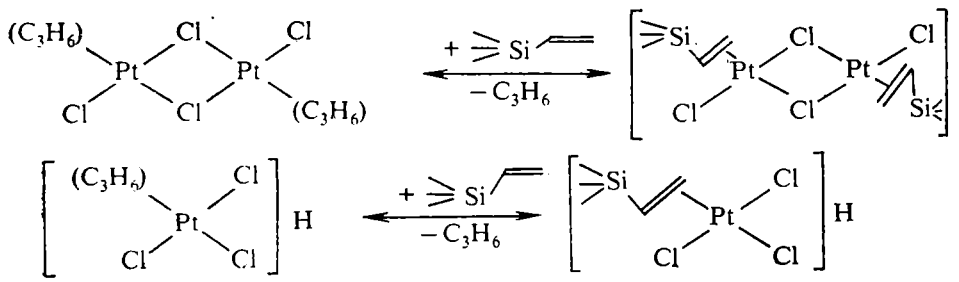
The mechanism of hydrosilylation involving Si-substituted vinylsilanes (25) can be represented in the following way:

(a) stabilization of the propylene complex of chloroplatinic acid as dimer XIV or hydroform XV:

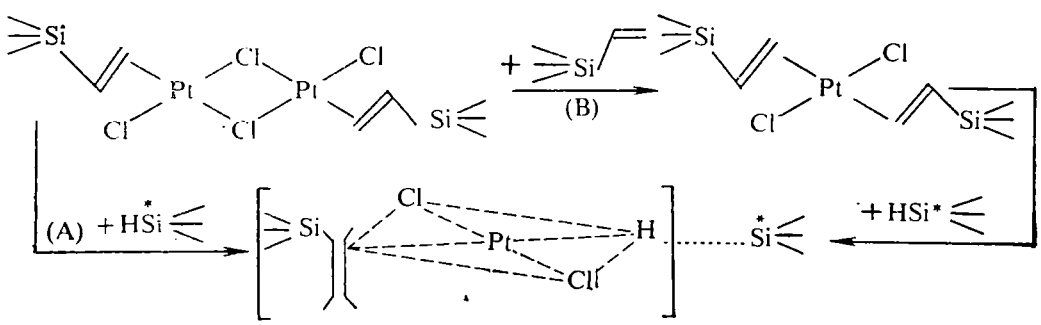


XIV XV

(b) displacement of the propylene from these complexes under the action of vinylsilane:

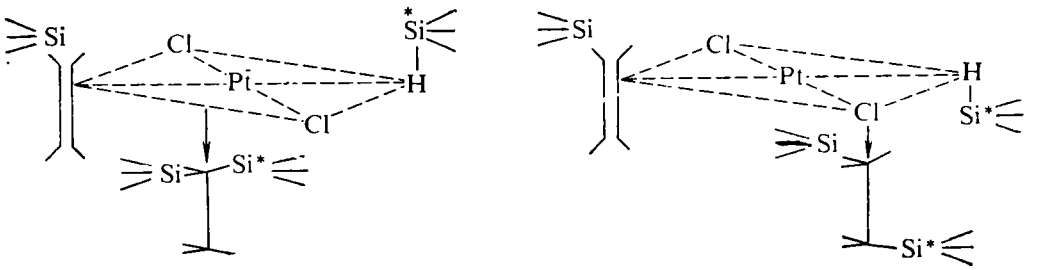


(c) cleavage by hydrosilane of the Pt—Cl—Pt bridge bonds in the dimer to form intermediate XVI whose structure is similar to Zeise's salt:



XVI

Being in the outer sphere of intermediate XVI, the group $-R_3Si-$ in an R_3SiH molecule can, in the final analysis, migrate both to the α- and β-carbon of the vinyl group giving the α- and β-adducts, respectively:



Addition of hydrosilane yielding the β-adduct is favoured by virtue of the steric effect exerted by geminally located silyl and platinum groups. On the other hand, when electron-seeking substituents, Cl, $CH_2=CH$, are available at the silicon in a molecule of the resulting vinylsilane, polarization of the double bond is less pronounced, and in the intermediate the platinum coordinates not only to the α- but also to the β-carbon of the double bond. As a result, the products of α-addition are formed, which has been observed in the experiment.

A study into reaction (26) has revealed that along with the vinyl group being exchanged for the methyl group or hydrogen an exchange occurs involving other substituents at the silicon, namely $CH_2=CH$ for Cl, CH_3 for $CH_2CH_2SiMe_kCl_{3-k}$, and Cl for $CH_2CH_2SiMe_kCl_{3-k}$ (k = 0-3).

The resulting novel organosilicon compounds containing the Si—H bond or the group $Si—CH=CH_2$ also undergo hydrosilylation to give a number of reaction products. For instance, apart from the major adduct $(CH_3)_3SiCH_2CH_2Si(CH_3)Cl_2$ (60%), the reaction between methyldichlorosilane and trimethylvinylsilane resulted in identification of $(CH_3)_3SiCH_2CH_2Si(CH_3)_3$ (1.3%), $Cl_2(CH_3)SiCH_2CH_2Si(CH_3)Cl_2$ (18,7%), $[(CH_3)_3SiCH_2CH_2]_2Si(CH_3)Cl$ (0.3%), and $[Cl_2(CH_3)SiCH_2CH_2]_2Si(CH_3)_2$ (1.5%).

Exchange processes also occurred in the thermal reaction of trimethylvinylsilane with 1-trimethylsilyl-2-methyldichlorosilylethane, giving $(CH_3)_3SiCl$ (1.8%), $CH_2=CH(CH_3)_2SiCH_2CH_2Si(CH_3)Cl_2$ (5.0%), $CH_2=CH(CH_3)_2SiCH_2CH_2Si(CH_3)_2CH=CH_2$ (3.9%), $Cl(CH_3)Si[CH_2CH_2Si(CH_3)_3]_2$ (0.1)% and $(CH_3)_2Si[CH_2CH_2Si(CH_3)Cl_2]_2$ (0.9%).

In explaining the formation pathways of the derivatives of 1,2-bis-silylethane and 1,4,7-trisilylheptane, allowance should also be

made for the ability detected in a symmetric Si-substituted 1,2-disilylethane to disproportionate even in the absence of Speier's catalyst. To illustrate, thermal conversions of $(CH_3)_3Si-CH_2CH_2Si(CH_3)Cl_2$ yield $Cl(CH_3)_2SiCH_2CH_2Si(CH_3)Cl_2$ (6.9%), $Cl(CH_3)Si[CH_2CH_2Si(CH_3)_3]_2$ (1.5%), $(CH_3)_3SiCH_2CH_2Si(CH_3)_2Cl$ (7,4%), $Cl_2Si[CH_2CH_2Si(CH_3)_3]_2$, $(CH_3)_2SiCl$ (0.5%), and $(CH_3)_3SiCl$ (0.2%).

In summary, hydrosilylation of Si-substituted vinylsilanes in the presence of Speier's catalyst causes both the starting reactants and the main reaction products to exchange substituents.

2.4. Some Reactions Involving $(CH_2 = CH)_n(CH_3)_{3-n}SiH$

In the $CH_2=CH(CH_3)_2SiX$ molecule, the vinyl group can activate the Si—X bond not only when X = Cl but also when X = H. For example, the compounds of the series $(CH_2=CH)_n(CH_3)_{3-n}SiH$ (n = 1-3) react readily with the aqueous-tetrahydrofuran solutions of alkali to give corresponding disiloxanes in 90% yield [21]:

$$2(CH_2=CH)_n(CH_3)_{3-n}SiH + H_2O \xrightarrow{OH^-} [(CH_2=CH)_n(CH_3)_{3-n}Si]_2O + H_2 \quad (27)$$

At the same time, under identical conditions, similar phenyl derivatives remain unchanged. Their conversion into corresponding disiloxanes occurs only on addition of ethyl alchohol. This must be due to the greater nucleophilicity of the ion $C_2H_5O^-$ against HO^-.

The Si—H bond in $(CH_2=CH)_n(CH_3)_{3-n}SiH$ has proved to be reactive towards vinyl- or phenylmagnesium chloride in THF. This reaction yielding a new Si—C bond proceeds as shown:

$$(CH_2=CH)_n(CH_3)_{3-n}SiH + RMgCl \rightarrow (CH_2=CH)_n(CH_3)_{3-n}SiR \quad (28)$$

$R = C_6H_5$, $CH_2=CH$; $n = 0$-3, $n = 1$-3

In the series $(CH_2=CH)_n(CH_3)_{3-n}Si-H$, an increase in the number of vinyl groups (n) in the molecule decreases the yield of corresponding chlorine derivatives in reaction with thionyl chloride. (In the case of trivinylsilane the yield of trivinylchlorosilane is as low as 40%).

Similarly, the reducing power of the Si—H bond declines with an increasing number of related vinyl groups in the molecule and in a high-temperature reaction whereby chloromethyltrichlorosilane is reduced to methyltrichlorosilane [21]:

$$(CH_2=CH)_n(CH_3)_{3-n}SiH + Cl_3SiCH_2Cl \xrightarrow{500\ ^\circ C} \rightarrow (CH_2=CH)_n(CH_3)_{3-n}SiCl + CH_3SiCl_3 \quad (29)$$

$n = 1$-3

For instance, at n = 3 the yield of trivinylchlorosilane is a mere 40%, whereas with $(C_6H_5)_n(CH_3)_{3-n}SiH$ the corresponding derivatives have been obtained in yields of 75-95%.

2.5. Chemical Conversions of Si-substituted 3,3-Difluoroallylsilanes [22]

Si-Substituted 3,3-difluoroallylsilanes exhibit high thermal stability, decomposing only at about 600 °C to form primarily the corresponding derivatives of vinylsilane and tetrafluoroethylene:

$$Cl_2(CH_3)SiCH_2XH{=}CF_2 \xrightarrow{600\ ^\circ C} Cl_2(CH_3)SiCH{=}CH_2 + CF_2{=}CF_2 \quad (30)$$

When nucleophilic and electrophilic reactants act on 3,3-difluoroallylchlorosilane only Si—Cl bonds enter into the reaction:

$$Cl_2(CH_3)SiCH_2CH{=}CF_2 \xrightarrow{+LiAlH_4} H_2(CH_3)\,SiCH_2CH{=}CF_2 \quad (31)$$

$$3CH_3MgI + Cl_3SiCH_2CH{=}CF_2 \rightarrow (CH_3)_3SiCH_2CH{=}CF_2 + 3MgClI \quad (32)$$

$$2CH_3OH + Cl_2(CH_3)\,SiCH_2CH{=}CF_2 \rightarrow CH_3(CH_3O)_2SiCH_2CH{=}CF_2 + 2HCl \quad (33)$$

$$H_2O + 2Cl(CH_3)_2SiCH_2CH{=}CF_2 \rightarrow O[CF_2{=}CHCH_2(CH_3)_2Si]_2 + 2HCl \quad (34)$$

$$SbF_3 + Cl_2(CH_3)SiCH_2CH{=}CF_2 \rightarrow F_2(CH_3)SiCH_2CH{=}CF_2 + SbFCl_2 \quad (35)$$

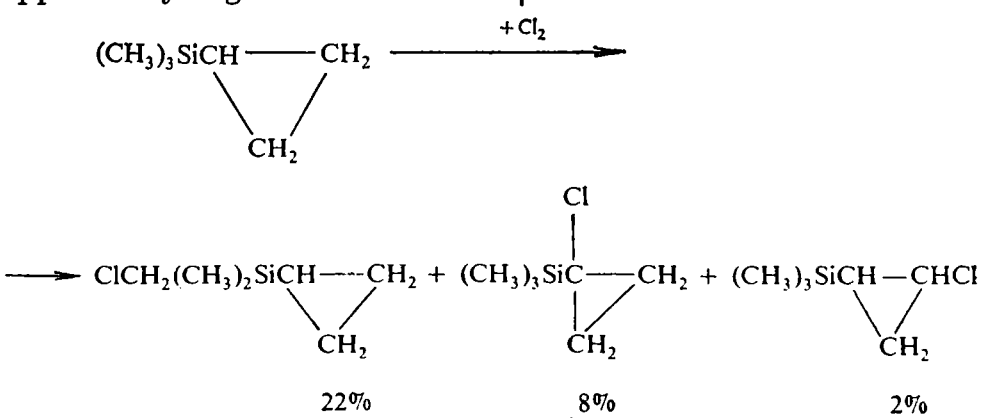
Addition of hydrogen iodide yields a γ-adduct, which is in contrast to corresponding allylsilane derivatives giving, with HI, β-adducts:

$$Cl_2(CH_3)SiCH_2CH{=}CF_2 + HI \rightarrow Cl_2(CH_3)SiCH_2CH_2CF_2I \quad (36)$$

This indicates opposite polarization of the double bond in the groups $>SiCH_2CH{=}CF_2$ and $>SiCH_2CH{=}CH_2$.

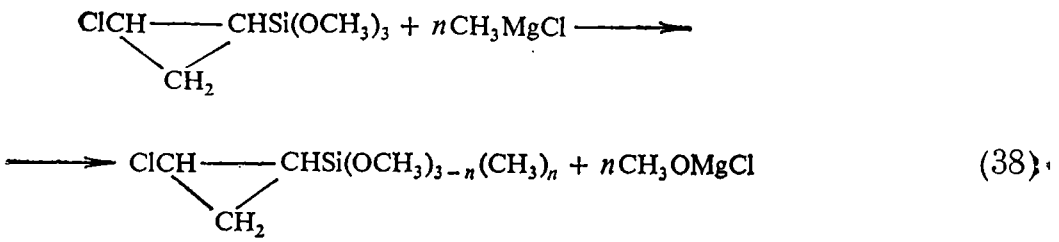
2.6. Chemical Conversions of Si-substituted Cyclopropylsilanes [20]

Chlorination of trimethylcyclopropylsilane with gaseous chlorine leads to substitution both in a cyclopropyl and methyl groups, the yield of trimethyl(α-chlorocyclopropyl)silane being appreciably higher than that of β-isomer:



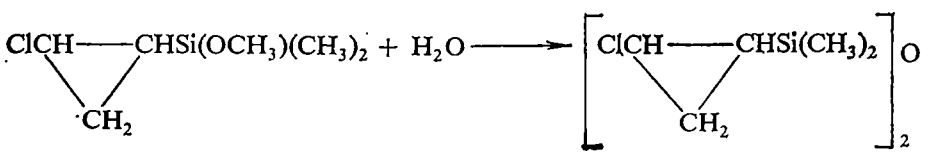
(37)

Methylation of 2-chlorocyclopropyltrimethoxysilane with a Grignard reagent brings about a partial or complete substitution of the methoxygroup:

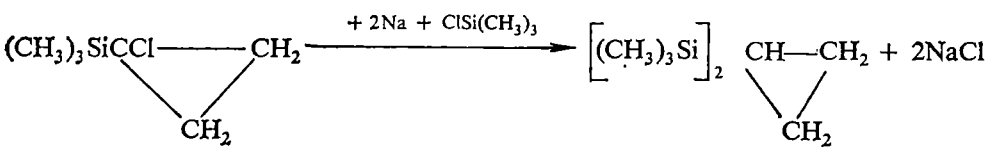


n = 2-3

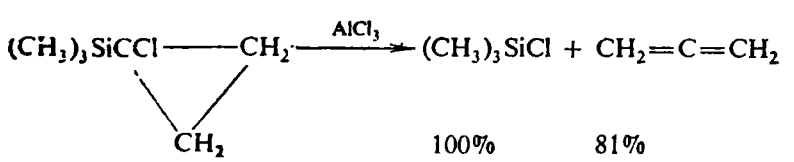
The resulting compound with $n = 2$ is converted to the corresponding disiloxane by hydrolysis:

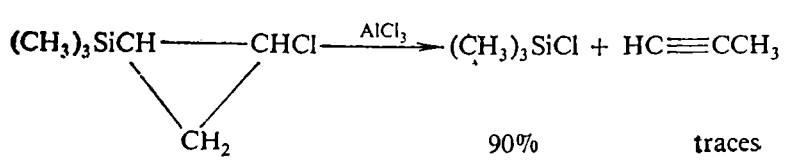


Trimethyl-1-chlorocyclopropylsilane reacts with sodium and trimethylchlorosilane to produce 1,1-bis(trimethylsilyl)cyclopropane

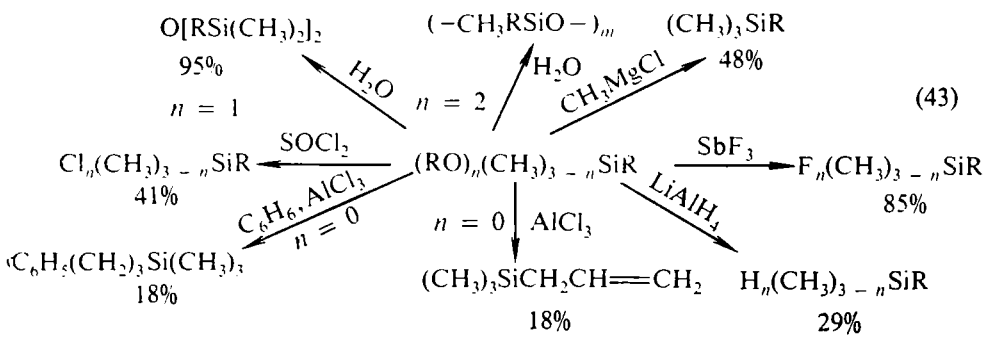


Exposure of 1- or 2-chlorocyclopropyltrimethylsilane to aluminium chloride results in the reaction of α- and β-decomposition, respectively:





Other chemical transformations of methyl(cyclopropyl)alkoxysilanes are shown schematically below:

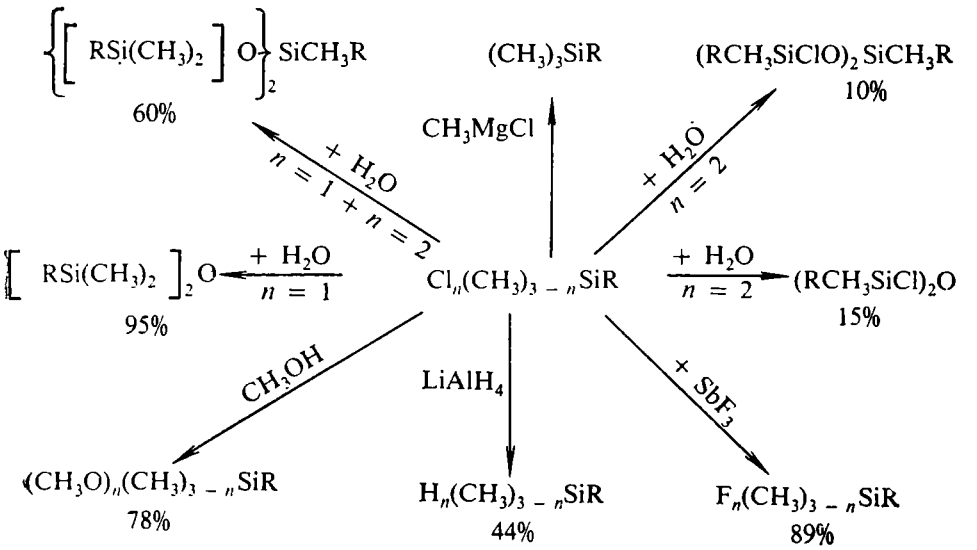


(43)

R = —CH(CH2)CH2

2.7. Chemical Conversions of Si-substituted 2,2-Difluorocyclopropylsilanes [24]

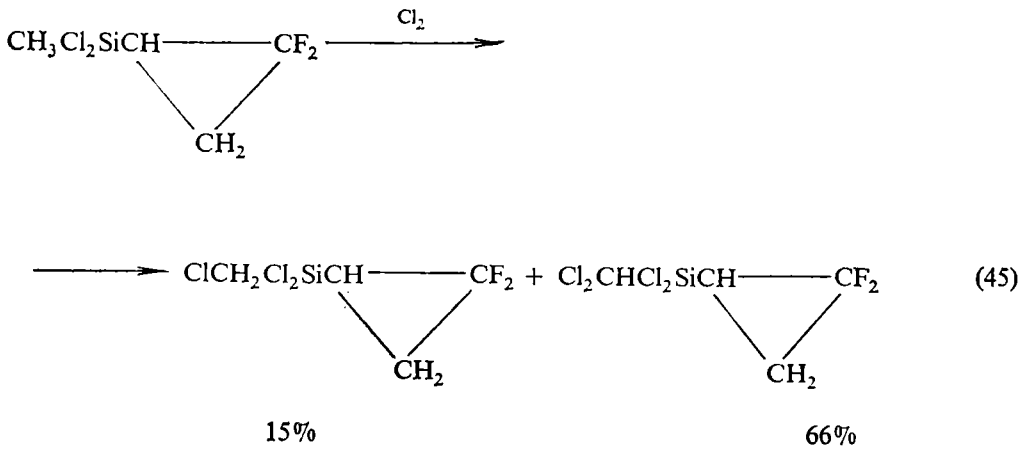
Reaction of methyl(2,2-difluorocyclopropyl)chlorosilanes with electrophilic and nucleophilic reagents does not cause their β-decomposition. Here only Si—Cl bonds enter into reaction as illustrated below:



(44)

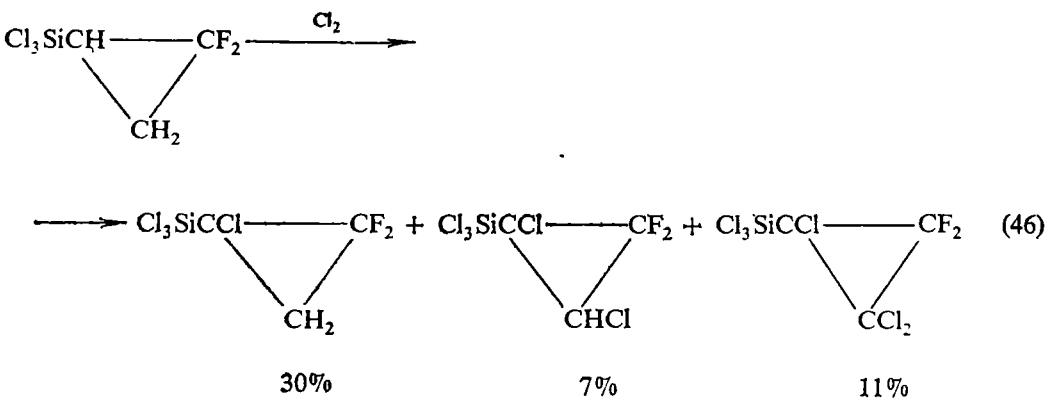
R = —CH(CF2)CH2

During chlorination of methyl(2,2-difluorocyclopropyl)dichlorosilane, the methyl group mainly undergoes the reaction:



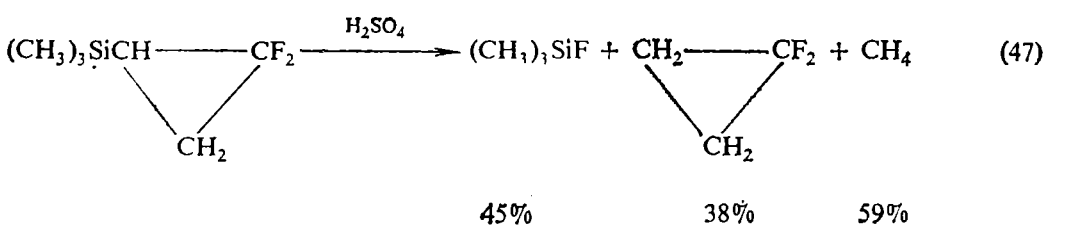
(45)

The cyclopropane ring is chlorinated only under severe conditions:



(46)

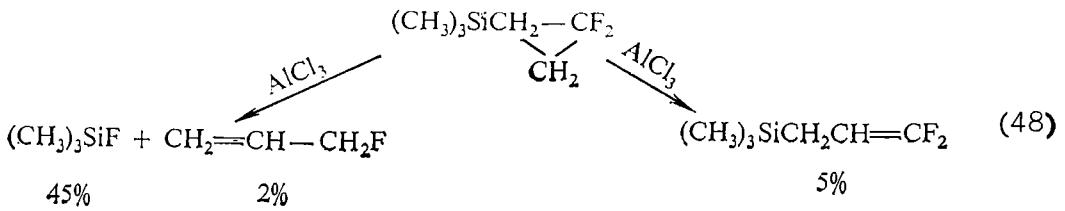
Sulphuric acid acts on trimethyl(2,2-difluorocyclopropyl)silane to form trimethylfluorosilane, which can be regarded as a product of β-decomposition:



(47)

A β-elimination reaction takes place when trimethyl(2,2-difluorocyclopropyl)silane is heated together with aluminium chloride.

Yet, even in this case, the process does not proceed selectively and is attended by the formation of trimethyl(3,3-difluoroallyl)silane.

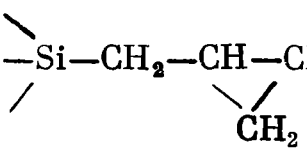


(48)

3. SPECTROSCOPIC STUDIES INTO SYNTHESIZED COMPOUNDS

A study has been made into the IR and Raman spectra of Si-substituted 2,2-difluorocyclopropylsilanes and 3,3-difluoroallylsilanes, and the most characteristic vibrational frequencies have been assigned [26]. It was established that the fluorine or chlorine atoms bonded to a cyclopropane ring have been found to react with the silicon atoms.

The UV spectra of peralkyl Si-substituted vinyldisilane have shown maximum absorption to shift to the longwave region, as compared with the corresponding derivatives of vinylsilane. This can be attributed to the effect of σ,π-conjugation between C=C and Si—Si bonds [25].

The electron absorption spectra of the charge-transfer complexes of (cyclopropylmethyl)silane derivatives suggest the presence of the σ,π-conjugation effect in the  group.

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12 Sulphur-containing Organosilicon Compounds

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1. COMPOUNDS CONTAINING THE Si—S BOND

The high reactivity of the Si—S bond [1, 2] makes it possible to employ Si—S-containing organosilicon compounds as synthons, which allows one to introduce the sulphur atom into a variety of organic and organometallic compounds, as well as to synthesize several classes of Si-functional organosilicon derivatives. As an example, the photochemical addition of trialkylsilylalkanethiols to monosubstituted acetylenes offers a convenient way of obtaining previously unknown trialkyl(alken-1-ylthio)silanes [3, 4]:

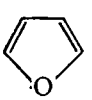
$$R^1_3SiSH + HC \equiv CR^2 \xrightarrow{h\nu} R^1_3SiSCH{=}CHR^2 \qquad (1)$$

This free-radical reaction is also initiated by azobisisobutyronitrile [3]. In this case the adducts involving a mixture of *cis*- and *trans*-isomers are obtained in yields as high as 80%. Reaction (1) is the first example that illustrates the addition of trimethylsilanethiols to unsaturated compounds (so-called silylthiylation). Addition of trialkylsilanethiols to aziridine has for the first time permitted these previously unknown 1-(trialkylsilylamino)-2-(trialkylsilylthio)ethanes to be synthesized [5]:

$$2R_3SiSH + \underset{\diagdown\,NH\,\diagup}{CH_2{-}CH_2} \rightarrow R_3SiNHCH_2CH_2SSiR_3 + H_2S \qquad (2)$$

Dialkylbis(2-furfurylthio)silanes have been prepared for the first time by reacting furfurylmercaptan with dialkyldichlorosilanes in the presence of pyridine [6]:

$$R_2SiCl_2 + 2HSCH_2C_4H_3O + 2C_5H_5N \longrightarrow$$
$$\longrightarrow R_2Si(SCH_2C_4H_3O)_2 + 2C_5H_5N \cdot HCl \qquad (3)$$
$$R = CH_3,\ C_2H_5,\ CH_2C_4H_3O{=}CH_2$$



The above products can be synthesized via the reaction between dialkyldichlorosilanes and sodium furfurylmercaptide:

$$R_2SiCl_2 + 2NaSCH_2C_4H_3O \rightarrow R_2Si(SCH_2C_4H_3O)_2 + 2NaCl \qquad (4)$$

Reaction (5) involves S—C bond cleavage in mono- and dialkenyl sulphides by hydrosilanes using a palladium catalyst that was obtained in situ from $PdCl_2(C_6H_5CN)_2$ and $P(C_6H_5)_3$ is a novel original route to produce compounds containing the Si—S bond. Triorganyl-(alkylthio)silanes, hexaorganyldisilthianes, as well as triogranyl-(vinylthio)silanes and previously unknown triogranyl(allylthio)silanes [7-9] have been prepared in this way:

$$X_3SiH + CH_2=CH(CH_2)_nSR \xrightarrow{(C_6H_5)_3P\cdot PdCl_2(NCC_6H_5)_2} \rightarrow X_3SiSR + H(CH_2)_nCH=CH_2 \quad (5a)$$

$$X_3SiSR + HSiX_3 \xrightarrow{(C_6H_5)_3P\cdot(NCC_6H_5)_2PdCl_2} X_3SiSSiX_3 + HR \quad (5b)$$

$X = C_2H_5$, C_2H_5O; $R = C_2H_5$, C_3H_7, $CH=CH_2$, $-CH_2-CH_2=CH_2$; $n = 0.1$

In this case, only those S—C bonds in organyl(alkenyl)sulphides which are conjugated with a double bond, i.e. those in the α,β- or β,γ-position with respect to the sulphur atom undergo cleavage.

Trialkyl(alkylthio)silanes readily react with trialkyl(alkoxy)stannanes and germanes to exchange an alkylthio for alkoxyl group [10]:

$$R^1_3SiSR^2 + R^3OMR^4_3 \rightarrow R^1_3SiOR^3 + R^2SMR^4_3 \quad (6)$$

$M = Sn$, Ge

The reaction does not proceed in the opposite direction. In contrast, the reaction of trialkylhalosilanes with trialkyl(alkylthio)stannanes affords trialkyl(alkylthio)silanes [11]:

$$R^1_3SiX + R^2SSnR^3_3 \rightarrow R^1_3SiSR^2 + XSnR^3_3 \quad (7)$$

A similar reaction between trialkylhalosilanes and O,O-dialkyl-S-trialkylstannyldithiophosphates leads to O,O-dialkyl-S-trialkylsilyldithiophosphates [12]:

$$R^1_3SiX + R^2_3SnSPS(OR^3)_2 \rightarrow R^1_3SiSPS(OR^3)_2 + XSnR^3_3 \quad (8)$$

This type of the exchange reaction allowed trialkyl(alken-1-ylthio)-silanes to be synthesized from readily available corresponding trialkyl(alken-1-ylthio)stannanes [13-16]:

$$R^1_3SiX + R^2CH=CHSSnR^3_3 \rightarrow R^1_3SiSCH=CHR^2 + XSnR^3_3 \quad (9)$$

$X = I$

R_3SiX with X = F, Cl, Br do not enter into reaction (9). Trialkyl(alken-1-ylthio)silanes can also be synthesized by the reaction between trialkylchlorosilanes and alken-1-ylthioacetates and dispersed sodium in ether [7]:

$$4R^1_3SiCl + 2R^2CH=CHSC(O)CH_3 + 4Na \rightarrow 2R^1_3SiSCH=CHR^2 + \\ + R^1_3SiOC(CH_3)=C(CH_3)OSiR^1_3 + 4NaCl \quad (10)$$

The reaction between trialkylchlorosilanes and trialkyl(acetylthio)-stannanes does not give the expected trialkyl(acetylthio)silanes but rather the isomeric trialkyl(thioacetoxy)silanes [17]:

$$R^1_3SiCl + R^2_3SnSC(O)CH_3 \rightarrow R^1_3SiOC(S)CH_3 + ClSnR^3_3 \quad (11)$$

The high Si—S bond reactivity, which drastically distinguishes it from the siloxane Si—O bond [18, 19], is due to a considerably lower energy (54 and 110-120 kcal/mole, respectively) and virtual lack of donor-acceptor interaction between silicon and sulphur in the ground state of the molecule. It has been reported [20-23] that the agreement of the force constant of this bond in trialkylsilanethiols, hexaalkyldisilthianes, and 1,1,3,3-tetramethylcyclodisilthiane ($K_{Si-S} = 2.28$ mdyn/Å), with that theoretically calculated for a single Si—S bond (2.22 mdyn/Å) indicates that the bond order between the silicon and sulphur atoms is practically equal to unity. Accordingly, the silicon atom in the $C_6H_5SSiR_3$ molecule does not possess withdrawing properties in respect to the sulphur atom in the ground state. At the same time, when the molecule is in the excited state, the Si—S bond order increases. This is evidenced by a hypsochromic shift of n-σ^* transitions in the ultraviolet spectra of hexaalkyldisilthianes and 1,3-dithia-2-silacycloalkanes [25]. The ionization potentials of trimethyl(butylthio)silane and hexamethyldisilthiane, calculated from the spectra of the charge-transfer complexes involving tetracyanethylene [26] can be accounted for in a similar way.

The electronic structure of the Si—S bond in trialkyl(alkylthio)-silanes and hexaalkyldisilthianes has been studied by infrared and ultraviolet spectroscopy and dipole moment technique. Analogous methods have been applied to the elucidation of the properties of isostructural carbon, germanium, and tin compounds [27-30]. The data obtained indicate that the Si—S bond order increases when molecules are in the excited state. However, in the ground state, the outer AOs of the silicon atom interact less effectively with the lone electron pair of the sulphur atom, as compared to the vacant AOs of germanium and tin. This seems to be responsible for the lability of the Si—S bond and the stability of Ge—S and, especially, Sn—S bonds.

The basicity of organic compounds of the Group IVA elements, that contain Si—O—C, Ge—O—C, Sn—O—C, Si—S—C, Ge—S—C, Sn—S—C, Si—O—Si, Ge—O—Ge, Sn—O—Sn, Si—S—Si, Ge—S—Ge, Sn—S—Sn, Si—O—Sn, Si—S—Sn groups, provides evidence that the withdrawing properties of the trialkylsilyl group in hexaalkyldisilthianes are much less pronounced than in hexaalkyldisiloxanes. In the case of $R_3GeSGeR_3$ and $R_3SnSSnR_3$, an inverse relationship has been observed. The electron-acceptor properties of the R_3M group in the ground state diminish with varying M in the following order: Sn > Ge ≫ Si. In the excited state, this order is reversed: Si > Ge > Sn, and the Si—S bond exhibits maximum polarity.

The spectroscopic basicity ($\Delta\nu$OH) of $R^1_3SiSCH{=}CHR^2$ and their saturated analogues, $R^1_3SiSCH_2CH_3$, indicates that the sulphur atom in compounds of the first type acts as an electron donor

with respect to both the silicon atom and the double bond. The double bond in the IR spectra of alkylsilyl(alken-1-ylthio)silanes [30] $R_3^1SiSCH{=}CHR^2$, absorbs in the same region (1570 to 1590 cm^{-1}) and shows the same integral intensity as it does in the IR spectra of alkylvinylsulphides [30]. The stretching frequency of the Si—S bond (630 cm^{-1}) in the IR spectra of trialkyl(alken-1-ylthio)silanes is independent of the nature of the alkyl substituents attached to the silicon atom [30].

2. COMPOUNDS CONTAINING THE Si—O—S BOND

Of the organosilicon compounds containing the Si—O—S bond, bis(trimethylsilyl)sulphate (BTS), a silylating and sulphonating agent, occupies a special place. Extensive studies of its properties have revealed new applications for this organosilicon synthon [31].

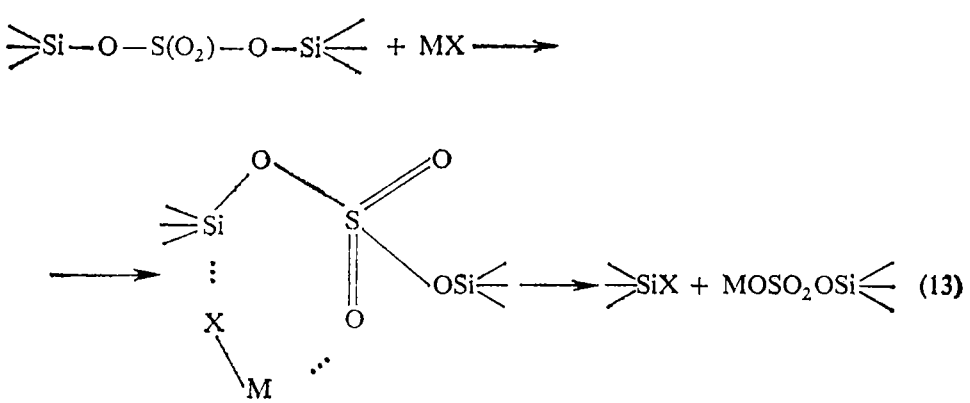
The reaction between BTS and salts of inorganic and organic acids provides a synthetic route to several Si-functional derivatives of trimethylsilane [32]. For instance, cleavage of BTS with alkali fluorides, chlorides, and bromides gives the corresponding trimethylhalosilanes [32]:

$$[(CH_3)_3SiO]_2SO_2 + 2MX \rightarrow 2(CH_3)_3SiX + M_2SO_4 \qquad (12)$$

X = F, Cl, Br, $-ONO_2$, CN, SCN, $OCOCH_3$, $OCOCF_3$;

M = Na, K

Reaction (12) seems to proceed through an intermediate six-membered active complex



(13)

and so on.

The reactivity of potassium halides drops in the order: F > Cl > Br.

Trimethyliodine cannot be prepared in a similar way due to an oxidation process

$$[(CH_3)_3SiO]_2SO_2 + 2KI \rightarrow [(CH_3)_3Si]_2O + I_2 + K_2SO_3 \qquad (14)$$

A similar redox process is observed when BTS reacts with hydrogen iodide [33]:

$$[(CH_3)_3SiO]_2SO_2 + 2HX \rightarrow (CH_3)_3SiOSi(CH_3)_3 + I_2 + SO_2 + H_2O \quad (15)$$

X = I, Br

BTS reacts with hydrogen bromide to form trimethylbromosilane in 40 % yield. The process is reversible and can be accompanied, as in the case of HI, by an oxidation process to liberate bromine as in (15) [33].

The reaction of BTS with sodium acetate and trifluoroacetate takes place according to Eq. (12) to give corresponding trimethylacyloxysilanes in 40% yield.

The reaction between BTS and nitrates goes according to scheme (12), and provides a straightforward and convenient means to synthesize previously unavailable trimethylsilylnitrate [32, 34, 35].

BTS is readily cleaved with ammonium thiocyanate and alkali cyanides to yield trimethylisothiocyanato- and trimethylcyanosilanes, respectively [32-36]. This route is the simplest and most convenient for the preparative synthesis of the latter.

The reaction between BTS and urea readily gives trimethylisocyanatosilane in high yield [37]:

$$[(CH_3)_3SiO]_2SO_2 + 2H_2NC(O)NH_2 \rightarrow 2(CH_3)_3SiNCO + (NH_4)_2SO_4 \quad (16)$$

BTS does not react with sodium sulphide at 180 °C. The redox reaction occurs at 225 °C [32]:

$$[(CH_3)_3SiO]_2SO_2 + Na_2S \rightarrow [(CH_3)_3Si]_2O + Na_2SO_3 + S \quad (17)$$

The reaction between BTS and alkali sulphates [38] readily converts the latter to persulphates:

$$[(CH_3)_3SiO]_2SO + M_2SO_4 \rightarrow [(CH_3)_3Si]_2O + M_2S_2O_7 \quad (18)$$

The yield of persulphates increases with increasing the ionic radius of the alkali metal (potassium, rubidium, and cesium sulphates are most reactive).

BTS is cleaved by the Group IB and IIB metal oxides [39]:

$$[(CH_3)_3SiO]_2SO_2 + M_nO \rightarrow [(CH_3)_3Si]_2O + M_nSO_4 \quad (19)$$

$n = 1, 2$

This reaction proceeds with particular ease when M = Zn and Hg. The reaction between BTS and HgO is very vigorous at 150 °C and involves not only cleavage of Si—O—S bonds, but also a partial rupture of the Si—C bonds to form sulphur dioxide, metallic mercury and ethane along with hexamethyldisiloxane and mercury sulphate [39].

BTS does not react with oxides of metals belonging to Groups IIA, IIIA, and IVA of the periodic table. Below 150 °C, BTS is not reactive

towards metal peroxides, such as Na_2O_2 and BaO_2. Higher temperatures result in hexamethyldisiloxane which must be decomposition product of the intermediate hexamethyldisilperoxane formed in the first step [39]:

$$[(CH_3)_3SiO]_2SO_2 + Na_2O_2 \xrightarrow[-Na_2SO_4]{} (CH_3)_3SiOOSi(CH_3)_3 \rightarrow$$
$$\rightarrow [(CH_3)_3Si]_2O + 0.5O_2 \quad (20)$$

The reaction with PbO_2, V_2O_5, and MnO_2 follows a similar scheme.

The reaction between BTS and thionyl chloride offers a convenient means to prepare trimethylsilylchlorosulphonate [40].

$$[(CH_3)_3SiO]_2SO_2 + SOCl_2 \rightarrow (CH_3)_3SiOSO_2Cl + (CH_3)_3SiCl + SO_2 \quad (21)$$

BTS is not only an efficient silylating but also sulphurizing agent which readily converts aromatic and heterocyclic compounds to the corresponding sulpho acids [41]:

$$RH + [(CH_3)_3SiO]_2SO_2 \rightarrow RSO_3H + (CH_3)_3SiOSi(CH_3)_3 \quad (22)$$
$$R = 4\text{-}CH_3C_6H_4,\ 4\text{-}H_2NC_6H_4,\ 4\text{-}(CH_3)_2NC_6H_4,\ 4\text{-}CH_3OC_6H_4,\ SC_4H_3$$

The reaction of BTS with pyridine leads to pyridinesulphotrioxide in 72% yield and is of preparative importance.

$$C_5H_5N + [(CH_3)_3SiO]_2SO_2 \rightarrow C_5H_5NSO_3 + (CH_3)_3SiOSi(CH_3)_3 \quad (23)$$

BTS is thermally stable and withstands prolonged heating even up to 150 °C. Evidence from differential thermal analysis suggests that BTS starts to decompose at 150 to 170 °C, whereas complete decomposition occurs at 192 to 200 °C. Hexamethyldisiloxane, trimethylsilylmethylsulphonate $(CH_3)_3SiOSO_2CH_3$ and tetramethyl-1,2-(mesiloxy)disiloxane $[CH_3SO_2O(CH_3)_2Si]_2O$ have been identified among the decomposition products [42].

Triethylsilane dissolves in sulphuric acid readily and completely to liberate hydrogen and to convert to bis(triethylsilyl)sulphate and hexaethyldisiloxane [43]. This reaction is catalyzed by mercury salts:

$$2(C_2H_5)_3SiH + H_2SO_4 \xrightarrow{Hg^{++}} [(C_2H_5)_3SiO]_2SO_2 + H_2 \quad (24)$$

3. COMPOUNDS CONTAINING THE $Si-(C)_n-S$ MOIETY

3.1. Synthesis and Properties of Triorganylsilylorganylthiols

Organosilicon compounds containing a thiol group in a hydrocarbon radical attached to the silicon atom are of certain theoretical and synthetic interest. Si-functional compounds of this type have gained a particular practical significance. Yet no conve-

nient synthetic routes have been reported prior to our investigations.

We have developed several simple effective procedures to synthesize trialkoxysilylalkanethiols.

For example, the reaction between chloroalkyl(trialkoxy)silanes and sodium hydrosulphide in a flow of hydrogen sulphide in dry alcohol at 30 to 40 °C has led to trialkoxysilylalkanethiols in 75-80% yields [44]:

$$(RO)_3Si(CH_2)_nCl + NaSH \xrightarrow{ROH} (RO)_3Si(CH_2)_nSH + NaCl \quad (25)$$

$R = CH_3,\ C_2H_5;\ n = 1,\ 3$

Bis(trialkoxysilylalkyl)sulphides $(RO)_3Si(CH_2)_nS(CH_2)_nSi(OR)_3$ are the by-products of reaction (25).

The photochemical reaction involving alkenyl(trichloro)silanes and thiolacetic acid has proved to be a convenient way of obtaining trichlorosilylalkanethiolacetates [43]:

$$Cl_3Si(CH_2)_nCH=CH_2 + HSCOCH_3 \xrightarrow{h\nu} Cl_3Si(CH_2)_nSCOCH_3 \quad (26)$$

$n = 0,\ 1$

The subsequent reaction between trichlorosilylalkanethiolacetates and alcoholic urea solution containing catalytic amounts of a metal alkoxide yields the corresponding thiols:

$$Cl_3Si(CH_2)_nSCOCH_3 + 4ROH + 3H_2NC(O)NH_2 \xrightarrow{RO^-}$$
$$\rightarrow (RO)_3Si(CH_2)_nSH + ROCOCH_3 + 3H_2NC(O)NH_2 \cdot HCl \quad (27)$$

$R = CH_3,\ C_2H_5;\ n = 2,\ 3$

Another convenient way to trialkoxysilylalkanethiols in 90% yield is the reaction of chloroalkyl(trialkoxy)silanes with thiolacetic acid in the presence of urea as an acceptor of hydrogen chloride followed by cleavage of the thiolacetate formed according to scheme [27]:

$$(RO)_3Si(CH_2)_nCl + HSCOCH_3 + H_2NC(O)NH_2 \rightarrow$$
$$\rightarrow (RO)_3Si(CH_2)_nSCOCH_3 + H_2NC(O)NH_2 \cdot HCl \quad (28)$$

Trialkoxy- and trialkylsilylalkanethiols can also be synthesized by the reaction of the corresponding chlorine derivatives with sodium thiolacetate in alcoholic sodium alkoxide.

$$X_3Si(CH_2)_nCl + NaSCOCH_3 \xrightarrow{ROH} X_3Si(CH_2)_nSCOCH_3 \xrightarrow{ROH}$$
$$\rightarrow X_3Si(CH_2)_nSH + ROCOCH_3 \quad (29)$$

$X = CH_3,\ C_2H_5,\ CH_3O,\ C_2H_5O;\ n = 1,\ 3$

Hydrosilylation of allylmercaptan with triethyl- and triethoxysilane in the presence of $H_2PtCl_6 \cdot 6H_2O$, $(C_6H_5)_3P_3RhCl$, $Co_2(CO)_8$, $(C_6H_5CN)_2PdCl_2 \cdot P(C_6H_5)_3$ proceeds in all cases to a small extent,

and the yields of 3-triorganylsilylpropanethiols do not exceed 2 to 3% [7]:

$$X_3SiH + CH_2{=}CHCH_2SH \rightarrow X_3SiCH_2CH_2CH_2SH \quad (30)$$

Reaction (30) is attended by several processes; namely,

dehydrocondensation

$$X_3SiH + HSCH_2CH{=}CH_2 \rightarrow X_3SiSCH_2CH{=}CH_2 + H_2 \quad (31)$$

the formation of diallyldisulphide is likely to follow the scheme

$$CH_2{=}CHCH_2SH + X_3SiSCH_2CH{=}CH_2 \rightarrow (CH_2{=}CHCH_2S)_2 + X_3SiH \quad (32)$$

hydrogenation

$$(CH_2{=}CHCH_2S)_2 + 2H_2 \rightarrow (CH_3CH_2CH_2S)_2 \quad (33)$$

disproportionation of X_3SiH

$$nX_3SiH \rightarrow (n-1)X_4Si + X_{4-n}SiH_n \quad (34)$$

$n = 2, 3, 4$

1-(Mercaptoalkyl)silatranes were first synthesized by transesterification of trialkoxysilylalkanethiols with tris(2-hydroxyalkyl)-amine [45]:

$$HS(CH_2)_nSi(OR)_3 + (HOCHRCH_2)_3N \rightarrow HS(CH_2)_nSi(OCHRCH_2)_3N + 3HOR \quad (35)$$

Previously unknown trialkyl(mercaptoalkylethynyl)silanes were obtained when reacting chloro derivatives with sodium hydrosulphide [46, 47]:

$$R^1_3SiC{\equiv}CCH(R^2)Cl + NaSH \rightarrow R_3SiC{\equiv}CCH(R^2)SH + NaCl \quad (36)$$

$R^1 = CH_3$, C_2H_5; $R^2 = H$, CH_3

The corresponding sulphides $R^1_3SiC{\equiv}CCH(R^2)SCH(R^2)C{=}CSiR^1_3$ are the by-products of reaction (36).

These silylacetylene thiols have also been prepared from corresponding thiocyanates

$$R^1_3SiC{\equiv}CCH(R^2)Cl + NaSCN \rightarrow NaCl + R^1_3SiC{\equiv}CCH(R^2)SCN \xrightarrow{+BrMgC_2H_5}$$

$$\rightarrow C_2H_5CN + R^1_3SiC{\equiv}CCH(R^2)SMgBr \xrightarrow{+H_2O} R^1_3SiC{\equiv}CCH(R^2)SH + HOMgBr \quad (37)$$

The synthesis of 4-trialkylsilylthiophenols in 50% yield has been carried out by reacting elemental sulphur with 4-trialkylsilylphenylmagnesiumbromide [48]:

$$4\text{-}R_3SiC_6H_4MgBr \xrightarrow{+S} 4\text{-}R_3SiC_6H_4SMgBr \xrightarrow{+HOH} 4\text{-}R_3SiC_6H_4SH + HOMgBr \quad (38)$$

$R = CH_3$, C_2H_5

The acidity of 4-trimethylsilylthiophenol does not differ much from that of thiophenol (pK_a = 11.09 and 10.94, respectively) [48]. The IR spectra of 4-trialkylsilylthiophenols and triorganylsilylalkanethiols exhibit an absorption band, ν_{SH}, at 2580 cm^{-1} (R = alkyl). The ultraviolet spectra of $R_3Si(CH_2)_nSH$ (n = 2, 3) are similar to the spectrum of ethanethiol and show the absorption maximum in the region 195 to 199 nm [49]. In the UV spectrum of trialkylsilylmethanethiols (n = 1), the absorption peak is shifted to the short-wave region and has a shoulder at 200 nm.

The dipole moments of trialkylsilylalkanethiols with n = 1-3 do not vary a great deal (1.51-1.57 D) and only slightly exceed the dipole moments of alkanethiols (1.48 D) [49].

Triorganylsilylalkanethiols also hardly differ from isostructural alkanethiols in their chemical properties. They add readily to alkylvinyl ethers and vinyl(trialkylsilylalkyl)sulphides by both an electrophilic and a radical mechanism. In the first case the reaction is catalyzed by sulphur dioxide, while in the latter it is initiated by traces of atmospheric oxygen [46, 47, 50]:

$$R^1SH + CH_2{=}CHXR^2 \begin{cases} \xrightarrow{SO_2} CH_3CH(XR^2)SR^1 \\ \xrightarrow{O_2} R^1SCH_2CH_2XR^2 \end{cases} \quad (39)$$

X = O, S; $R^1 = R^3_3Si(CH_2)_n$, $R^4_3SiC{\equiv}CCHR^5$; $R^2 = C_4H_9$, $(CH_2)_nSiR^3_3$

The photochemical addition of trialkylsilylalkanethiols to allyl alcohol and dimethyl(vinyl)ethynylcarbinol occurs readily [51, 52]:

$$R_3Si(CH_2)_nSH + CH_2{=}CHCH_2OH \xrightarrow{h\nu} R_3Si(CH_2)_nSCH_2CH_2CH_2OH \quad (40)$$

$$R_3Si(CH_2)_nSH + CH_2{=}CHC{\equiv}C{-}C(CH_3)_2OH \xrightarrow{h\nu}$$

$$\rightarrow R_3Si(CH_2)_nSCH_2CH_2C{\equiv}C{-}C(CH_3)_2OH \quad (41)$$

R = CH_3, C_2H_5; n = 1-3

The thermal addition of trialkoxysilylalkanethiols to divinyl sulphide leads to new organosilicon monomers, i.e. vinyl(2-trialkoxysilylalkylthioethyl)sulphides [53]:

$$(RO)_3Si(CH_2)_nSH + CH_2{=}CHSCH{=}CH_2 \xrightarrow{\Delta}$$

$$\rightarrow (RO)_3Si(CH_2)_nSCH_2CH_2SCH{=}CH_2 \quad (42)$$

R = CH_3, C_2H_5; n = 1-3

In this case the reactivity of the trialkoxysilylalkanethiols depends on the number of methylene groups (n) separating the silicon and sulphur atoms. The reactivity drops with increasing n. Attempts to obtain diadducts by the reaction between trialkoxysilylalkanethiols and divinyl sulphide have failed.

In nucleophilic conditions, trialkyl- and trialkoxysilylalkanethiols readily add to acetylene in dioxane at 25 atm and 30 to 80 °C to form vinyl(triorganylsilylalkyl)sulphides [54-58]: .

$$X_3Si(CH_2)_nSH + HC{\equiv}CH \xrightarrow{RO^-} X_3Si(CH_2)_nSCH{=}CH_2 \quad (43)$$

$X = CH_3$, C_2H_5, C_3H_7, CH_3O, C_2H_5O; $n = 1\text{-}3$

In addition to vinyl(triorganylsilylalkyl)sulphides, this reaction yields diadducts, 1,2-bis(triorganylsilylalkylthio)ethanes. As with reaction (42), here too, a greater reactivity is shown by trialkylsilylmethanethiols ($n = 1$) which undergo vinylation even at 30 °C.

It is only at 30 atm and 100 to 110 °C that addition of 4-trialkylsilylthiophenols to acetylene can be achieved [48]:

$$4\text{-}R_3SiC_6H_4SH + HC{\equiv}CH \xrightarrow{RO^-} 4\text{-}R_3SiC_6H_4SCH{=}CH_2 \quad (44)$$

Unlike alkanethiols, addition of trialkylsilylalkanethiols to phenylacetylene results in a mixture of *cis*- and *trans*-adducts (4 : 1) [59]:

$$R_3Si(CH_2)_nSH + HC{\equiv}CC_6H_5 \xrightarrow{RO^-} R_3SiCH{=}CHC_6H_5 \quad (45)$$

Formation of the *trans*-adducts is due to the thermal rearrangement of the *cis*-isomers during distillation.

The nucleophilic addition of trialkylsilylalkanethiols to diacetylene in dioxane with a catalytic amount of potassium hydroxide at −10 to +40 °C produces previously unknown (1-trialkylsilylalkylthio)-buten-1-ines-3 in 72-78% yields [60]:

$$R_3Si(CH_2)_nSH + HC{\equiv}C{-}C{\equiv}CH \xrightarrow{HO^-} R_3Si(CH_2)_nSCH{=}CH{-}C{\equiv}CH \quad (46)$$

$R = CH_3$, C_2H_5; $n = 1\text{-}3$

A more convenient method of obtaining the latter, including those compounds that contain alkoxyl groups at silicon, is the addition of trialkyl- and trialkoxysilylalkanethiols to diacetylene in liquid ammonia at −30 °C [61].

A nucleophilic addition of triorganylsilylalkanethiols to divinylsulphoxide proceeds in its own special fashion to form vinyl(triorganylsilylalkyl)sulphides $X_3Si(CH_2)_nSCH{=}CH_2$ instead of the expected product, vinyl(triorganylsilylalkylthioethyl)sulphoxides [62]. The resulting compounds are the products of the thermal decomposition of the intermediate adducts [63]:

$$X_3Si(CH_2)_nSH + H_2C{=}CHSOCH{=}CH_2 \rightarrow [X_3Si(CH_2)_nSCH_2CH_2SOCH{=}CH_2] \rightarrow$$

$$\rightarrow X_3Si(CH_2)_n{-}S{-}\underset{\displaystyle H\cdots\cdots O}{\overset{\displaystyle CH_2}{CH}}{-}S{-}CH{=}CH_2 \rightarrow$$

$$\rightarrow X_3Si(CH_2)_nSCH{=}CH_2 + CH_2{=}CHSOH \quad (47)$$

This reaction is a unique method for the indirect vinylation of thiols [64] and has now found application in organic synthesis [65]. Reaction (47) is accompanied by a number of side processes [63]. To illustrate, the redox reaction of vinyl sulphenic acid and divinylsulphoxide with triorganylsilylalkanethiols yields vinyl(triorganylsilylalkyl)disulphides, bis(triorganylsilylalkyl)disulphides, and divinylsulphide:

$$X_3Si(CH_2)_nSH + HOSCH{=}CH_2 \rightarrow X_3Si(CH_2)_nSSCH{=}CH_2 + H_2O \quad (48)$$

$$X_3Si(CH_2)_nSH + H_2C{=}CHSOCH{=}CH_2 \rightarrow$$

$$\rightarrow X_3Si(CH_2)_nSS(CH_2)_nSiX_3 + H_2C{=}CHSCH{=}CH_2 + H_2O \quad (49)$$

The presence of 1,1-bis(triorganylsilylalkylthio)- and 1-vinylthio-(2-triorganylsilylalkylthio)ethanes in the reaction mixture is attributed to the secondary thiylation of the generating vinyl(triorganylsilylalkyl)sulphides and divinylsulphide:

$$X_3Si(CH_2)_nSH + H_2C{=}CHS(CH_2)_nSiX_3 \rightarrow [X_3Si(CH_2)_nS]_2CHCH_3 \quad (50)$$

$$X_3Si(CH_2)_nSH + H_2C{=}CHSCH{=}CH_2 \rightarrow X_3Si(CH_2)_nSCH_2CH_2SCH{=}CH_2 \quad (51)$$

The nucleophilic reaction of trialkylsilylalkanethiols with 2-chloroethanol and 2-chloroethylvinyl ether has proved to be a convenient method to synthesize trialkylsilylalkylthioethanols and their vinyl ethers [51, 66]:

$$R^1_3Si(CH_2)_nSH + ClCH_2CH_2OR^2 \xrightarrow[-HCl]{} R^1_3Si(CH_2)_nSCH_2CH_2OR^2 \quad (52)$$

$R^1 = CH_3,\ C_2H_5;\ R^2 = H,\ -CH{=}CH_2$

The reaction between trialkylsilylalkanethiols and epichlorohydrin in the presence of KOH has permitted previously unknown (trialkylsilylalkylglycidyl)sulphides to be obtained [67]:

$$R_3Si(CH_2)_nSH + ClCH_2CH\!\!-\!\!CH_2 + KOH \rightarrow$$

$$\rightarrow R_3Si(CH_2)_nSCH_2CH\!\!-\!\!CH_2 + KCl + H_2O \quad (53)$$

$R = CH_3,\ C_2H_5;\ n = 1\text{-}3$

The nucleophilic reaction of benzenesulphochloride with sodium trialkylsilylalkylthiolate is complicated by a side redox process which leads to a non-separable mixture of S-aryl(S′-trialkylsilylalkyl)thiosulphonates and S,S′-bis(trialkylsilylalkyl)disulphides [68]:

$$R_3Si(CH_2)_nSNa + ClSO_2C_6H_5 \rightarrow R_3Si(CH_2)_nSSO_2C_6H_5 + NaCl \quad (54)$$

$$R_3Si(CH_2)_nSSO_2C_6H_5 + NaS(CH_2)_nSiR_3 \rightarrow [R_3Si(CH_2)_nS]_2 + C_6H_5OSONa \quad (55)$$

$R = CH_3,\ C_2H_5;\ n = 1\text{-}3$

The use of a large excess of sulphochloride stops the process at the stage of formation of thiosulphonates. The latter are exceedingly labile and decompose when attempts are made to isolate them individually:

$$R_3Si(CH_2)_nSSO_2(CH_2)_nSiR_3 \rightarrow R_3Si(CH_2)_nS(CH_2)_nSiR_3 \quad (56)$$

Triorganylsilylalkanethiols are readily oxidized to the corresponding disulphides by iodine in alcohol or benzene in the presence of sodium alkoxide or trialkylamine [69]:

$$2X_3Si(CH_2)_nSH + I_2 \xrightarrow[-2HI]{} X_3Si(CH_2)_nSS(CH_2)_nSiX_3 \quad (57)$$

$X = CH_3$, C_2H_5, CH_3O, C_2H_5O; $n = 1\text{-}3$

Like alkanethiols, triorganylsilylalkanethiols react with $TiCl_4$ to form complexes of composition 1 : 1 and 2 : 1, and react readily with organic and inorganic mercurials to yield the corresponding mercury derivatives [49, 70]:

$$R_3Si(CH_2)_nSH + XHgY \rightarrow R_3Si(CH_2)_nSHgY + HX \quad (58)$$

$R = C_2H_5$, CH_3O; $X = Cl$, I, C_6H_5, CH_3COO;

$Y = Cl$, I, CH_3, C_6H_5, $OCOCH_3$; $n = 1\text{-}3$

Reaction (58) offers considerable scope for obtaining novel biologically active monomers, in particular, mercurothioalkyl(trialkoxy)-silanes.

The reaction of trialkyl(mercaptoalkylethynyl)silanes with mercuric chloride proceeds quantitatively and has been used for their analytical determination [46, 47]:

$$R^1_3SiC{\equiv}CCHR^2SH + HgCl_2 \rightarrow R^1_3SiC{\equiv}CCHR^2SHgCl + HCl \quad (59)$$

In contrast to numerous carbofunctional organosilicon compounds containing the group XCH_2CH_2Si, triorganylsilylalkanethiols do not undergo β-decomposition. This can be attributed to the low electronegativity of the sulphur atom (2.66) [71]. For example, unlike 2-trialkylsilylethanols [72], 2-trialkylsilylethanethiols do not undergo β-decomposition with KOH (in the reaction involving acetylene).

3.2. Organosilicon Compounds Containing the C—S—C Group

The addition of hydrogen sulphide and thiols to triorganyl(alkenyl)- and triorganyl(alkynyl)silanes presents a convenient synthetic route to carbofunctional organosilicon compounds containing the C—S—C group.

Thus, the photochemical reaction of gaseous hydrogen sulphide with triorganyl(alkenyl)silanes carried out for the first time affords

smoothly bis(triorganylsilylalkyl)sulphides [73]. The reaction occurs via the intermediate formation of triorganylsilylalkanethiols as indicated below:

$$X_3Si(CH_2)_nCH{=}CH_2 + H_2S \xrightarrow{h\nu} X_3Si(CH_2)_{n+2}SH \xrightarrow{H_2C{=}CH(CH_2)_nSiX_3,\ h\nu} \rightarrow X_3Si(CH_2)_{n+2}S(CH_2)_{n+2}SiX_3 \quad (60)$$

$X{=}CH_3,\ C_2H_5,\ CH_3O,\ C_2H_5O;\ n{=}0,\ 1$

The photoinitiated addition of hydrogen sulphide to dimethyl(chloromethyl)vinylsilane and dimethyl(divinyl)silane turned out to be a convenient method of preparing previously unavailable thiasilacycloalkanes [74, 75]. Again, the reaction proceeds via the corresponding thiol intermediates:

$$ClCH_2(CH_3)_2SiCH{=}CH_2 + H_2S \xrightarrow{h\nu} ClCH_2(CH_3)_2SiCH_2CH_2SH \longrightarrow$$

$$\xrightarrow{h\nu} \text{(1-silacyclohexane-4-thiol)} \quad (61)$$

$$(CH_3)_2Si(CH{=}CH_2)_2 + H_2S \xrightarrow{h\nu} (CH_3)_2Si(CH{=}CH_2)CH_2CH_2SH \xrightarrow{h\nu}$$

$$\rightarrow \text{(1-silacyclohexane-3-thiol)} \quad (62a)$$

$$\rightarrow \text{(1,4-thiasilacycloheptane)} \quad (62b)$$

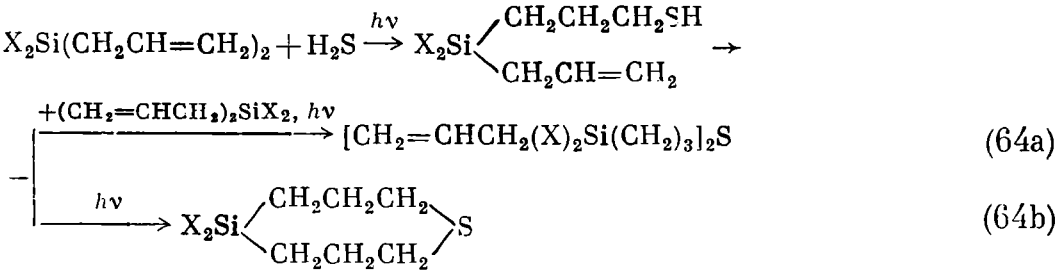
Along with the intramolecular thiylation of dimethyl(vinyl)(2-mercaptoethyl)silane (62a, b), its intermolecular addition to the starting dimethyl(divinyl)silane occurs to the corresponding sulphide:

$$CH_2{=}CH(CH_3)_2SiCH_2CH_2SH + CH_2{=}CH(CH_3)_2SiCH{=}CH_2 \xrightarrow{h\nu}$$

$$\rightarrow CH_2{=}CH(CH_3)_2SiCH_2CH_2SCH_2CH_2Si(CH_3)_2CH{=}CH_2 \quad (63)$$

The photochemical addition of gaseous hydrogen sulphide to Si-substituted diallylsilane proceeds in a similar manner [76, 77].

In this case, however, the intermolecular addition of the intermediate thiol to the initial Si-substituted diallylsilane prevails over intermolecular cyclization into the corresponding 1-thia-5-silacyclooctane:

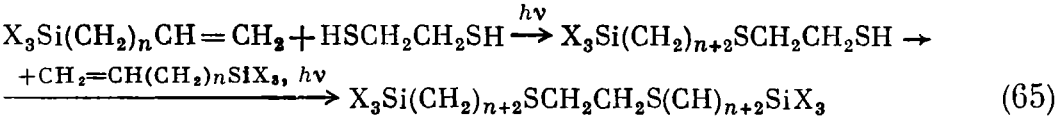


(64a)

(64b)

$X=CH_3$, CH_3O, F

The photochemical reaction of triorganyl(alkenyl)silanes and alkenyl(trichloro)silanes with 1,2-ethanedithiol leads to the corresponding mono- and, especially, diadducts [78]:

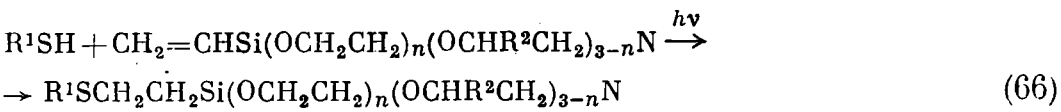


(65)

$X=CH_3$, C_2H_5, CH_3O, C_2H_5O, Cl; $n=0$, 1

If X is alkyl or alkoxyl, reaction (65) proceeds easily, and even 15 min after it has started the overall yield of the adducts is as high as 40 to 50%. At the same time, the reactivity of alkenyl(trichloro)silanes is much lower, which appears to be due to the lesser π-electron density of the double bond in the molecule.

The photochemical thiylation of 1-vinylsilatrane and its C-methylderivative with alkanethiols, α,ω-alkanedithiols, thiolcarboxylic acids, and the esters of mercaptoalkanecarboxylic acids, as well as 2-trimethoxysilylethanethiol and 1-(2-mercaptoethyl)-3-methylsilatrane proceeds rather easily and follows this general scheme [79]:



(66)

R^1=alkyl, $HS(CH_2)_m$, RCO, $ROCOCH_2$, $(CH_2)_3SiCH_2CH_2$, $N(CH_2CH_2O)_3SiCH_2CH_2$; $R^2=H$, CH_3

α,ω-Alkanedithiols react with 1-vynylsilatranes to form not only the mono-, but also the diadducts $N(CH_2CHR^2O)_{n-3}(CH_2CH_2O)_n \cdot SiCH_2CH_2S(CH_2)_mSCH_2CH_2Si(OCH_2CH_2)_n(OCHR^2CH_2)_{n-3}N$. In reaction (66), ethanethiol and 3,7,10-trimethyl-, 1-vinylsilatrane are most reactive.

The photochemical addition of alkanethiols to 1,2-bis(triorganylsilyl)ethylenes [80] proceeds at a much slower rate than that to

triorganyl(vinyl)silanes and 1-vinylsilatranes. This seems to be due to steric factors:

$$R^1SH + R^2_3SiCH{=}CHSiR^3_3 \xrightarrow{h\nu} R^2_3SiCH(SR^1)CH_2SiR^3_3 \quad (67)$$

In the case of unsymmetrical 1,2-bis(triorganylsilyl)ethylenes ($R^2 \neq R^3$), two adducts are formed in the ratio 1 : 1.

The photochemical addition of gaseous hydrogen sulphide to triorganyl(ethynyl)silanes [81, 82] occurs through intermediate triorganylsilylvinylthiols, and leads to previously unknown bis-(2-triorganylsilylvinyl)sulphides

$$R^1_2R^2SiC{\equiv}CH + H_2S \xrightarrow{h\nu} R^1_2R^2SiCH{=}CHSH \xrightarrow{HC\equiv CSiR^2R^1_2,\ h\nu}$$

$$\rightarrow R^1_2R^2SiCH{=}CHSCH{=}CHSiR^2R^1_2 \quad (68)$$

$R^1 = CH_3,\ C_2H_5;\quad R^2 = CH_3,\ OCH_3,\ OC_2H_5,\ OC_3H_7$

The photochemical reaction between alkanethiols and trialkyl-(ethynyl)silanes results both in mono- and diadducts [83, 84]:

$$R^1_3SiC{\equiv}CR^2 + HSR^2 \xrightarrow{h\nu} R^1_3SiCH{=}CHSR^2 \xrightarrow{+HSR^2,\ h\nu}$$

$$\rightarrow R^1_3SiCH_2CH(SR^2)_2 \quad (69a)$$

$$\rightarrow R^1_3SiCH(SR^2)CH_2SR^2 \quad (69b)$$

$R = CH_3,\ C_2H_5;\quad R = C_2H_5,\ C_3H_7\ \ C_4H_9,\ \ C(CH_3)_3$

The structure of the starting reactants is responsible for the ratio of 2,2- and 1,2-diadducts (reactions (69a) and (69b), respectively).

The UV-initiated addition of alkanethiols to triorganyl(organyl-ethynyl)silanes follows a similar pathway [85]:

$$R^1_3SiC{\equiv}CR^2 + HSR^3 \xrightarrow{h\nu} R^1_3SiCH{=}C(SR^3)R^2 \xrightarrow{+HSR^3,\ h\nu}$$

$$\rightarrow R^1_3SiCH(SR^3)CH(SR^3)R^2 \quad (70)$$

The photochemical or *tert*-butyl peroxide-initiated addition of 2-(diethylamino)ethanethiol to trialkyl(vinyl)silanes leads to 2-trialkylsilylethyl-2-(diethylaminoethyl)sulphides [86, 87]:

$$R_3SiCH{=}CH_2 + HSCH_2CH_2N(C_2H_5)_2 \xrightarrow{h\nu} R_3SiCH_2CH_2SCH_2CH_2N(C_2H_5)_2 \quad (71)$$

Besides, aminoalkyl(trialkylsilylalkyl)sulphides can be prepared from trialkylsilylalkanethiols according to the Mannich reaction [88, 89] or when they react with aziridine [90] or alkenylamines [91, 92].

A convenient method for obtaining alkyl(trialkoxysilylalkyl)-sulphides is the reaction of sodium alkanethiolates with trialkoxy-(haloalkyl)silanes [93]:

$$(R^1O)_3Si(CH_2)_nX + NaSR^2 \rightarrow (R^1O)_3Si(CH_2)_nSR^2 + NaX \quad (72)$$

$R^1 = CH_3,\ C_2H_5;\quad R^2 = C_2H_5,\ C_3H_7,\ C_4H_9;\quad X = Cl,\ Br;\quad n = 1\text{-}3$

Trialkoxy(halomethyl)silanes ($n = 1$) enter into reaction (72) most readily, and the chloro derivatives are less reactive than bromo derivatives.

Reaction (72) can be performed using sodium alkanethiolates in situ by adding metallic sodium to trialkoxy(haloalkyl)silane and alkanethiol in hexane:

$$(R^1O)_3Si(CH_2)_nX + HSR^2 + Na \rightarrow (R^1O)_3Si(CH_2)_nSR^2 + NaX + 0.5H_2 \quad (73)$$

Since methanethiol is not convenient to handle, trialkoxy(methylthioalkyl)silanes have been prepared by reacting sodium trialkoxysilylalkanethiolates with methyl iodide [93]:

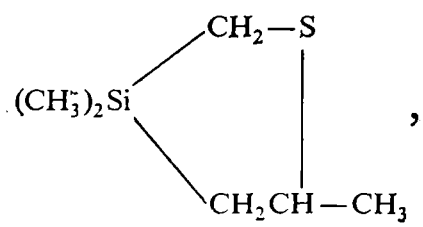
$$(R^1O)_3Si(CH_2)_nSNa + ICH_3 \rightarrow (R^1O)_3Si(CH_2)_nSCH_3 + NaI \quad (74)$$

The condensation of sodium 2-hydroxyethanethiolate with trialkoxy(chloromethyl)silane results in 2,2-dialkoxy-1-oxa-4-thia-2-silacyclohexanes [94]. The latter react with triethanolamine to give 1-(2'-hydroxyethylthiomethyl)silatrane.

The nucleophilic reaction of potassium hydrosulphide with dimethyl-bis(chloromethyl)silane produced the previously unknown 3,3-dimethyl-1-thia-3-silacyclobutane [95, 96]:

$$(CH_3)_2Si(CH_2Cl)_2 + KSH \rightarrow KCl + \left[(CH_3)_2Si\begin{matrix}CH_2SH\\CH_2Cl\end{matrix}\right] \xrightarrow{KSH} (CH_3)_2Si\begin{matrix}CH_2\\CH_2\end{matrix}S + KCl + H_2S \quad (75)$$

The reaction between potassium hydrosulphide and the dimethyl(ω-chloroalkyl)alkenylsilanes $Cl(CH_2)_nSi(CH_2)_mCH=CH_2$ ($n = 1$, $m = 1$; $n = 3$, $m = 0$) in alcohol is a convenient synthetic route to five- and six-membered C-methylsubstituted-Si-dimethylthiasilacycloalkanes:



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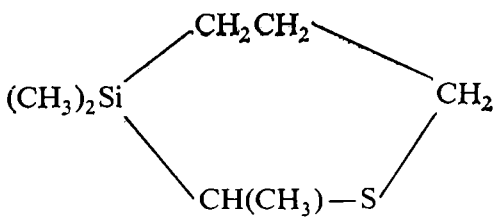
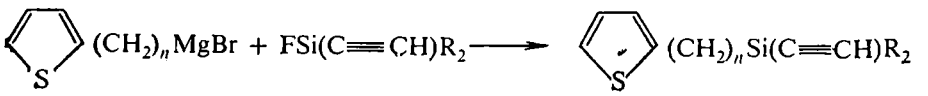


The reaction involves intermediate dimethyl(ω-mercaptoalkyl)alkenylsilanes. It was not possible to obtain thiasilacycloalkanes in a similar fashion using dimethyl(chloromethyl)vinylsilane ($n = 1$, $m = 0$) and dimethyl(chloropropyl)allylsilane ($n = 3$, $m = 1$), since the reaction ceased at the stage of formation of the corresponding thiols [96, 120, 121].

2-Thienylmagnesiumbromide and 2-thienylmethylmagnesiumbromide react with dialkyl(ethynyl)fluorosilanes to form 2-thienyl- or

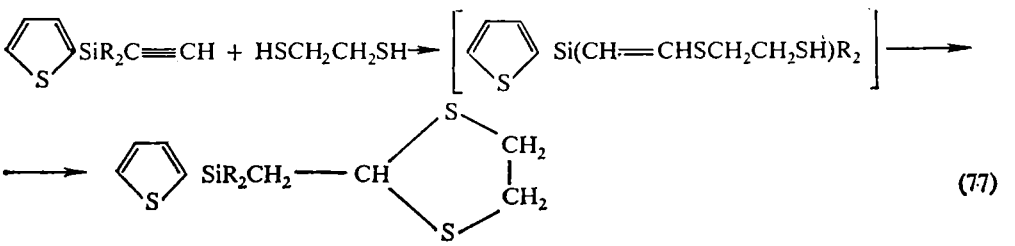
2-thienylmethyl(dialkyl)ethynylsilanes [97]:



(76)

R = CH_3, C_2H_5; n = 0, 1

The reaction of the former (n = 0) with 1,2-ethanedithiol gives rise to 2-[(2′-thienyl)dialkylsilylmethyl]-1,3-dithiolanes:



(77)

A series of 1-(organylthioalkyl)silatranes have been obtained by transesterification of the corresponding organylthioalkyl(trialkoxy)-silanes with triethanolamine [98, 99]:

$$R^1S(CH_2)_nSi(OR^2)_3 + (HOCH_2CH_2)_3N \rightarrow R^1S(CH_2)_nSi(OCH_2CH_2)_3N + 3HOR^2 \quad (78)$$

R = C_2H_5, C_3H_7, C_4H_9, CH_3CO

Similarly, the transesterification of bis(trialkoxysilylalkyl)sulphides led to bis(silatranylalkyl)sulphides [100]:

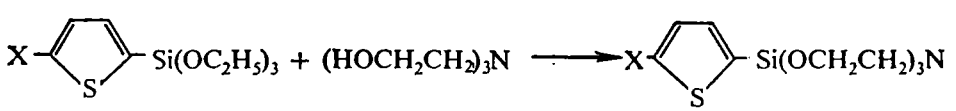
$$S[(CH_2)_nSi(OR)_3]_2 + 2(HOCH_2CH_2)_3N \rightarrow S[(CH_2)_nSi(OCH_2CH_2)_3N]_2 + ROH \quad (79)$$

The series of 1-(organylthioalkyl)silatranes has also been obtained by the reaction between organylthiolates of alkali metals and 1-(haloalkyl)silatranes [101, 102]:

$$RSM + X(CH_2)_nSi(OCH_2CH_2)_3N \rightarrow RS(CH_2)_nSi(OCH_2CH_2)_3N + MX \quad (80)$$

R = alkyl, aryl, CH_3CO, CN; M = Na, K; X = Cl, Br

The transesterification of 2-thienyl(triethoxy)silanes and their 5-substituted derivatives with triethanolamine has afforded 1-(2′-thienyl)silatranes and their 5-derivatives [103]:



(81)

X = H, Cl, Br, CH_3, CN

One of the most common methods for synthesizing organosilicon compounds of a variety of classes involves hydrosilylation [104, 105].

The hydrosilylation of the unsaturated sulphides $RS(CH_2)_nCH=CH_2$ with triethyl- and triethoxysilane in the presence of $H_2PtCl_6 \times 6H_2O$ or $[(C_6H_5)_3P]_3RhCl$ [106-110] proceeds in a non-regioselective fashion to form predominantly the terminal adduct according to the Farmer free-radical addition:

$$RS(CH_2)_nCH=CH_2 + HSiX_3 \rightarrow \begin{cases} RS(CH_2)_nCH_2CH_2SiX_3 \\ RS(CH_2)_nCH(CH_3)SiX_3 \end{cases} \quad (82)$$

$R = C_2H_5$, C_3H_7, $CH=CH_2$, $CH_2CH=CH_2$; $X = C_2H_5$, OC_2H_5; $n = 0, 1, 4$

The structure of both reactants is responsible for the overall yield of the adducts (20 to 80%) and the ratio of normal and abnormal products of reaction (82) (from 16 : 1 to 1 : 1). $Co_2(CO)_8$ does not catalyze reaction (82), whereas $(C_6H_5CN)_2PdCl_2 \cdot (C_6H_5)_3P$, as indicated in Sec. 2, merely brings about cleavage of the C—S bond.

The hydrosilylation of organyl(alkenyl)sulphides with triethyl- and triethoxysilane is accompanied by several secondary processes, however, to a small extent:

dehydrocondensation:

$$RS(CH_2)_nCH=CH_2 + HSiX_3 \rightarrow RS(CH_2)_nCH=CHSiX_3 + H_2 \quad (83)$$

hydrogenation:

$$RS(CH_2)_nCH=CH_2 + H_2 \rightarrow RS(CH_2)_nCH_2CH_3 \quad (84)$$

disproportionation of the starting triorganylsilane:

$$nX_3SiH \rightarrow (n-1)X_4Si + X_{4-n}SiH_n \quad (85)$$

$n = 4, 3, 2$

Polymerization of the starting organyl(alkenyl)sulphides:

$$mRS(CH_2)_nCH=CH_2 \rightarrow [RS(CH_2)_n\underset{|}{C}H-CH_2-]_m \quad (86)$$

Alongside these secondary processes that often accompany the hydrosilylation of unsaturated compounds, in the case of α,β- and β,γ-unsaturated sulphides, the cleavage of the C—S bonds in the initial organyl(alkenyl)sulphides occurs according to Eq. (5). For example, when triethylsilane reacts with divinylsulphide in the presence of $H_2PtCl_6 \cdot 6H_2O$, the C—S bond cleavage results in the corresponding triethyl(vinylthio)silane (27% yield) and even prevails over hydrosilylation processes (the total yield of the adducts being 20%). By contrast, with ethylvinylsulphide, the hydrosilylation reaction prevails and the C—S bond in ethyl(5-hexenyl)sulphide is not cleaved by triorganylsilanes at all.

The reaction between triethylsilane and ethylvinylsulphide is initiated by accelerated electrons [111] and leads to a mixture of

products of hydrosilylation and C—S bond cleavage in the starting sulphide.

The hydrosilylation of divinyl- and diallylsulphide ($n = 0, 1$) with diethylsilane in the presence of $H_2PtCl_6 \cdot 6H_2O$ and $[(C_6H_5)_3P]_3RhCl$ normally proceeds in a non-regioselective manner:

$$(C_2H_5)_2SiH_2 + [H_2C{=}CH(CH_2)_n]_2S \rightarrow$$

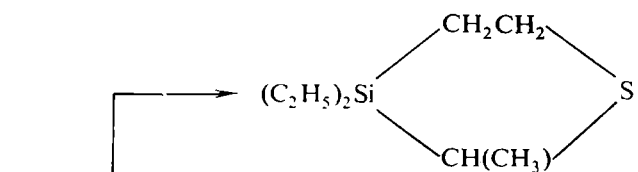
$$\rightarrow H(C_2H_5)_2Si(CH_2)_{n+2}S(CH_2)_n CH{=}CH_2 \quad (87a)$$

$$\rightarrow H(C_2H_5)_2SiCH(CH_3)(CH_2)_nS(CH_2)_nCHCH_2 \quad (87b)$$

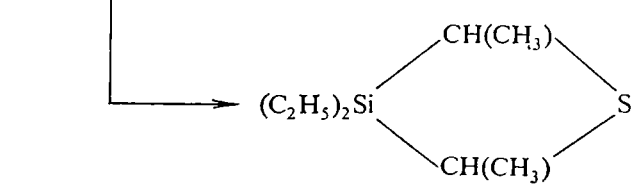
It is only diallylsulphide that reacts with diethylsilane in the presence of $[(C_6H_5)_3P]_3RhCl$ according to scheme (87a).

The addition of diethylsilane to divinyl- and diallylsulphide offers wide possibilities for the synthesis of four-, five-, and eight-membered thiasilacycloalkenes, since the monoadducts formed in the hydrosilylation undergo further cyclization as shown below:

$$(C_2H_5)_2SiH_2 + CH_2{=}CHSCH{=}CH_2 \longrightarrow$$

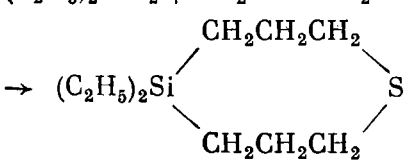


(88a)



(88b)

$$(C_2H_5)_2SiH_2 + CH_2{=}CHCH_2SCH_2CH{=}CH_2 \rightarrow$$



(89)

Here the cyclization of transient isomeric vinyl(diethylsilylethyl)-sulphides proceeds solely as α-addition (88a, b).

In contrast to this, allyl(diethylsilylpropyl)sulphide undergoes cyclization only according to the Farmer rule of free-radical addition, as shown in scheme (89).

Tris(triphenylphosphine)rhodium chloride is the most effective catalyst of the cyclization process (88, 89).

To settle the question concerning the mutual effect of silicon and sulphur in triorganyl(organylthioalkyl)silanes, extensive research has been made into their chemical conversions.

To illustrate, the thiylation reaction involving trialkyl(vinylthioalkyl)silanes can follow either an electrophilic or a homolytic mechanism. In the latter case, however, the process takes place more readily and is regiospecific [50]:

$$R^1_3Si(CH_2)_nSCH=CH_2+HSR^2 \rightarrow$$

$$\xrightarrow{H^+} R^1_3Si(CH_2)_nSCH(SR^2)CH_3 \qquad (90a)$$

$$\xrightarrow{O_2} R^1_3Si(CH_2)_nSCH_2CH_2SR^2 \qquad (90в)$$

A kinetic study of the hydrolysis of trialkyl(vinylthioalkyl)silanes, which proceed as follows:

$$R_3Si(CH_2)_nSCH=CH_2+H_2O \xrightarrow{H^+} R_3Si(CH_2)_nSH+CH_3CHO \qquad (91)$$

has established that the nucleophilicity of the double bond in these compounds is lower than in their oxygen analogues $R_3Si(CH_2)_nOCH=CH_2$ [114-117].

Trialkyl(vinylthioalkyl)silanes $R_3Si(CH_2)_nSCH=CH_2$ (n = 1-3) are readily polymerized in the presence of boron trifluoride etherate [118]. In this process, homologues with n = 2 undergo polymerization more reluctantly than the neighbouring members with n = 1 and 3. This can be attributed to the great strength of the catalyst-monomer complex.

1-(Organylthiomethyl)silatranes and bis(silatranylalkyl)sulphides react with organic and organosilicon C-halo derivatives to form easily the corresponding sulphonium salts [119]:

$$R^1X+R^2SCH_2Si(OCHR^3CH_2)_3N \rightarrow$$

$$\rightarrow X^-R^1R^2\overset{+}{S}CH_2Si(OCHR^3CH_2)_3N \qquad (92)$$

$R^3=H$, CH_3;

$X=Cl$, Br, I; $R^1=$alkyl, $CH_2Si(OCH_2CH_2)_3N$;

$R^2=$alkyl, C_5H_5, $C_6H_5CH_2$, $HOCOCH_2$

The unusually high reactivity of 1-(organylthiomethyl)silatra es and bis(silatranylmethyl)sulphides when reacting with halo derivatives is due to the greater nucleophilicity of the sulphur atom caused by a strong I effect of the silatranyl group σ^*-(—0.9)-(—1.2).

Using 1-(iodomethyl)- or 1-(bromomethyl)silatranes as halo derivatives in reaction (92) has enabled alkylbis(silatranyl)- and even tris(silatranyl)methylsulphonium halides to be synthesized. This process, however, proceeds only under rigid conditions at 130 to 140 °C.

The reaction between 1-iodomethylsilatrane and dimethylsulphide yields (dimethylsilatranylmethyl)sulphonium iodide:

$$(CH_3)_2S + ICH_2Si(OCH_2CH_2)_3N \rightarrow [N(CH_2CH_2O)_3SiCH_2\overset{+}{S}(CH_3)_2]I^- \quad (93)$$

Finally, sulphonium salts of 1-(organylthioalkyl)silatranes can also be synthesized by transesterification of the corresponding sulphonium salts of organylthioalkyl(trialkoxy)silanes:

$$X^-[R^1_2S(CH_2)_nSi(OR^2)_3] + (HOCH_2CH_2)_3N \rightarrow$$

$$\rightarrow X^-[R^1_2\overset{+}{S}(CH_2)_nSi(OCH_2CH_2)_3N] + 3R^2OH \quad (94)$$

Sulphonium salts of the type $[N(CH_2CH_2O)_3SiCH_2CH_2\overset{+}{S}R^1R^2]X^-$ are unstable and lend themselves readily to β-decomposition. These compounds can be obtained only by reacting 1-(2-organylthioethyl)-silatranes with methyl iodide in a solution of ether or hexane. In alcohol, they decompose completely. In contrast to organosilicon compounds that contain a Si—C—C—S group with a bivalent sulphur atom, the ready β-decomposition of these sulphonium salts is due to a sharp difference in the electronegativity of silatranyl and sulphonium group.

Alkyl(trialkoxysilylalkyl)sulphides add easily methyl iodide to yield the corresponding sulphonium salts:

$$(R^1O)_3Si(CH_2)_nSR^2 + ICH_3 \rightarrow [(R^1O)_3Si(CH_2)_n\overset{+}{S}(CH_3)R^2]I^- \quad (95)$$

When $R^1 = CH_3$, $R^2 = C_6H_5$, $n = 1$, the resulting sulphonium salt decomposes so that both $Si—CH_2$ and $S—CH_2$ bonds break:

$$[(CH_3)_3\overset{+}{S}]I^- + C_6H_5CH_2I$$

$$\uparrow \qquad \uparrow$$

$$+CH_3I \downarrow$$

$$[(CH_3)_2\overset{+}{S}CH_2C_6H_5]I^- + (CH_3O)_3SiCH_2I$$

$$\uparrow \qquad \uparrow$$

$$+CH_3I \downarrow \quad (a)$$

$$[(CH_3O)_3SiCH_2\overset{+}{S}(CH_3)CH_2C_6H_5]I^-$$

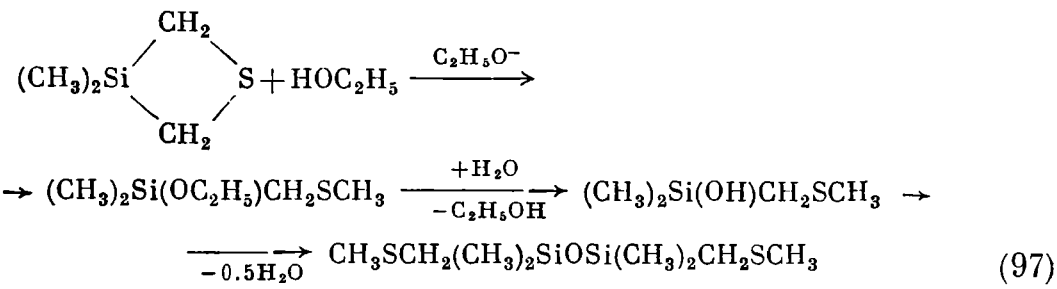
$$\downarrow \qquad \downarrow \quad (b)$$

$$(CH_3O)_3SiCH_2SCH_3 + C_6H_5CH_2I$$

$$+CH_3I \downarrow$$

$$[(CH_3O)_3SiCH_2\overset{+}{S}(CH_3)_2]I^- \quad (96)$$

The simple and convenient methods developed for synthesizing thiasilacyclanes have made it possible to elucidate the properties of these previously unknown heterocyclic compounds. For instance, 3,3-dimethyl-1-thia-3-silacyclobutane is readily cleaved by alcoholic alkali to give dimethyl(ethoxy)silylmethylsulphide and methyl-1,3-bis(methylthiomethyl)tetramethyldisiloxane [120]:

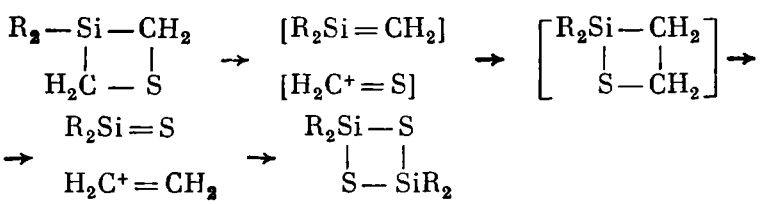


(97)

Treatment of 3,3-dimethyl-1-thia-3-silacyclobutane with alcoholic mercuric chloride also breaks the C—Si bond [120]. The reaction between 3,3-dimethyl-1-thia-3-silacyclobutane and methyl iodide also results in the ring opening involving C—S bond cleavage [121].

Unlike 1-thia-3-silacyclobutanes, its higher homologues react with $HgCl_2$ and CH_3I as do thiacycloalkanes to yield the corresponding adducts.

The thermal fragmentation of 2,4-dimethyl-3,3-diethyl-1-thia-3-silacyclobutane and 3,3-dimethyl-1-thia-3-silacyclobutane gives rise to the corresponding dialkylsilaethylenes and dialkylsilanethiones [122-124]. Similar intermediates were revealed in the fragmentation of the same heterocycles by electron impact and photoionization mass spectrometry [125].



(98)

According to photoionization mass spectrometry [124], decomposition of 1-thia-3-silacyclobutane derivatives which involves the formation of dialkylsilanethiones is more characteristic than fragmentation yielding 1,1-dialkylsilaethylenes. Therefore 3,3-dialkyl-1-thia-3-silacyclobutanes themselves can be recommended as sources of dialkylsilanethiones.

According to electron gas-phase diffraction [126], the molecule of 3,3-dimethyl-1-thia-3-silacyclobutane has a non-planar structure. The dihedral angle between the planes CSIC and CSC is 13° as compared with 34° between the C—Si—C and C—C—C planes in silacyclobutane, and 26° between C—C—C and CSC in thiacyclobutane.

Evidence from UV spectroscopy and electron absorption spectroscopy of charge transfer complexes (CTC with iodine and tetracyanoethylene) suggests that the dimethylsilyl group in thiasilacycloalkanes exhibits an electron-donating effect.

The UV spectra of 1,2-bis(trialkylsilylalkylthio)ethanes $R_3Si(CH_2)_nSCH_2CH_2S(CH_2)_nSiR_3$ with $n = 2$, 3 are nearly identical and have an absorption peak at 195 nm [49]. As in the case of trialkylsilylmethanethiols, the absorption maximum with $n = 1$ shows a shoulder in the range 200 to 210 nm [49]. When $n = 1$, $\mu =$ $= 1.77$D; when $n = 2$ and 3, $\mu = 1.95$-2.01D with due regard for free rotation $\mu_f = 2.18$D [49], the dipole moments of $R_3Si(CH_2)_n \cdot SCH_2CH_2S(CH_2)_nSiR_3$ are indicative of the small conformational mobility of their molecules. Substitution of one oxygen for one sulphur in the compounds completely provides for their conformational mobility (for $R_3Si(CH_2)_nSCH_2CH_2O(CH_2)_nSiR$, $\mu = 1.93$D; $\mu_f = 1.96$D).

1,2-Bis(trialkylsilylalkylthio)ethanes do not form complexes with pyridine. This indicates that their silicon exhibits no pronounced electrophilicity. At the same time, as with dialkylsulphides, they yield adducts with $TiCl_4$.

The spectroscopic basicity of the sulphur atom ($\Delta\nu$OH) in the series of organylthioalkyl(trialkoxy)silanes merely implies inductive interaction between the sulphur and silicon atoms [128].

The CTC spectra of organylthiomethyl(trialkoxy)silanes and 1-(organylthiomethyl)silatranes [129] with tetracyanethylene show that electron conjugation nN-σ (C=Si) = nS does occur in the latter. This accounts for more pronounced donor properties of the sulphur atom in 1-(organylthiomethyl)silatranes, as compared with (organylthiomethyl)trialkoxysilanes where the nS and σ(C—Si) orbitals are likely to interact but do not overlap with an nN-orbital.

^{1}H NMR spectroscopy has been used to study the proton shielding in fragments of the $RSCH_2Si(OC_2H_5)_3$ molecule, the corresponding silatranes $RSCH_2Si(OCH_2CH_2)_3N$, their sulphinyl derivatives $RS(O)CH_2Si(OCH_2CH_2)_3N$, and the cations $R(CH_3)\overset{+}{S}CH_2Si(OCH_2CH_2)_3N$ [130, 131]. The data obtained fit the scheme of hypervalent bonding in the X—Si ← N system of silatranes.

The degree of interaction between silicon and nitrogen increases with the increasing electronegativity of substituent X. This is re-

sponsible for the inconstant σ*-donor (—0.9)-(—1.2) ability of the silatranyl group $-Si(OCH_2CH_2)_3N$ [132, 133] as opposed to the triethoxysilyl group $\sigma^*(C_2H_5O)_3Si$-(—0.2). Furthermore, the ^1H PMR spectroscopy provides evidence for the conformational composition of these compounds. Specifically, 1-(organylsulphinylmethyl)silatranes and 1-(*tert*-butylthiomethyl)silatrane iodomethylate show a predominance of a conformer with the Si—C bond *trans*-oriented with respect to S=O and $S-C(CH_3)_3$ bonds. The advantage of such a conformation is due to its lower steric strain as compared with other possible structures.

The conformational isomerism and dipole moments of 1-(ethylthioalkyl)silatranes $C_2H_5S(CH_2)_nSi(OCH_2CH_2)_3N$ ($n = 1, 2$) have also been investigated using the Kerr constants [134].

The X-ray fluorescent K_α and K_β spectra of the sulphur atom in compounds of the type $RS(CH_2)_nSi(OR')_3$, $RS(CH_2)_nSi(OCH_2CH_2)_m \cdot [OCH(CH_3)CH_2]_{3-m}N$, and the cations $RR\overset{+}{S}(CH_2)_nSi(OCH_2CH_2)_m \cdot [OCH(CH_3)CH_2]_{3-m}N$ indicate a significant differences in the electronic structure of the CH_2SCH_2 moiety in organylthiomethyl(trialkoxy)silanes and 1-(organylthiomethyl)silatranes. A powerful $+I$ effect of the silatranyl group appears to be responsible for the modest positive charge ($\leqslant 0.1e^-$) of sulphur in the sulphonium salts of silatranes.

3.3. Compounds Containing the $Si—C_n—S=O$ Group

Several new organosilicon compounds containing the group $SiC_nS=O$ have been synthesized via oxidation of organosilicon thiols and sulphides. For example, treatment of trialkylsilylalkanethiols by 70% H_2O_2 yields trialkylsilylalkanesulphonic acids [136, 137]:

$$R_3Si(CH_2)_nSH + 3H_2O_2 \rightarrow R_3Si(CH_2)_nSO_3H + 3H_2O \quad (99)$$
$$n = 1\text{-}3$$

The resulting organosilicon sulphonic acids have been isolated either in the hydrated form $R_3Si(CH_2)_nSO_3H \cdot mH_2O$ ($m = 1, 2$), or as potassium or sodium salts.

Using less concentrated hydrogen peroxide solutions along with sulphonic acids results in S,S′-bis(trialkylsilylalkyl)disulphides and previously unknown S,S′-bis(trialkylsilylalkyl)thiosulphonates. These species are essentially the intermediates of the oxidation of trialkylsilylalkanethiols to the corresponding sulphonic acids:

$$2R_3Si(CH_2)_nSH \xrightarrow[-2H_2O]{H_2O_2} R_3Si(CH_2)_nSS(CH_2)_nSiR_3 \xrightarrow[-2H_2O]{+2H_2O_2}$$

$$\rightarrow R_3Si(CH_2)_nSO_2S(CH_2)_nSiR_3 \xrightarrow[-2H_2O]{+2H_2O_2}$$

$$\rightarrow R_3Si(CH_2)_nSO_2SO_2(CH_2)_nSiR_3 \xrightarrow{+H_2O_2} 2R_3Si(CH_2)_nSO_3H \qquad (100)$$

S, S′-Bis(triorganylsilylalkyl)thiosulphonates are thermally unstable and decompose when heated to give bis(triorganylsilylalkyl)sulphides and sulphur dioxide:

$$R_3Si(CH_2)_nSO_2S(CH_2)_nSiR_3 \xrightarrow{\Delta}$$
$$\rightarrow R_3Si(CH_2)_nS(CH_2)_nSiR_3 + SO_2 \qquad (101)$$

In the presence of pyridine, the vinyl(trialkylsilylalkyl)sulphides $R_3Si(CH_2)_nSCH=CH_2$ with $n = 2, 3$ are readily oxidized with 30% H_2O_2 to the corresponding sulphoxides, whereas with SeO_2, the 70% H_2O_2 oxidation yields sulphones [138]:

$$R_3Si(CH_2)_nSCH=CH_2 + H_2O_2 \rightarrow$$
$$\left\{\begin{array}{l} \xrightarrow{C_5H_5N} R_3Si(CH_2)_nS(O)CH=CH_2 + H_2O \\ \xrightarrow{SeO_2} R_3Si(CH_2)_nS(O_2)CH=CH_2 + H_2O \end{array}\right. \qquad (102)$$

Attempts to produce corresponding sulphoxides or sulphones, with $n = 1$, failed [138, 139]. Even under the mildest conditions, the reaction yields hexaalkyldisiloxane, acetaldehyde, and water-soluble polyalkylsiloxane containing sulpho-acid groups $[RSi(CH_2OSO_2H)-O-]_n$. A similar decomposition also follows, to a small degree, the oxidation of $R_3Si(CH_2)_nSCH=CH_2$ with $n = 2, 3$.

In the organosilicon chemistry, oxidative cleavage of the Si—C bond is of a general character and the presence of sulphur in the hydrocarbon radical attached to the silicon atom is not very important [140]. As an example, tetraethyl- and triethyl(chloromethyl)-silane are easily oxidized by a 30% H_2O_2 solution in acetic acid to yield a polymer, $C_2H_5SiO_{1.5} \cdot 3SiO_2 \cdot 2.5H_2O$, which indicates cleavage of more than one Si—C bond.

Finally, the oxidation of 1-(organylthioalkyl)silatranes with 30% H_2O_2 in alcohol has, for the first time, yielded 1-(organylsul-

phinylalkyl)silatranes [131]:

$$RS(CH_2)_nSi(OCH_2CH_2)_3N + H_2O \rightarrow$$
$$\rightarrow RSO(CH_2)_nSi(OCH_2CH_2)_3N + H_2O \quad (103)$$
$$R = \text{alkyl},\ C_6H_5,\ C_6H_5CH_2;\ n = 1\text{-}3$$

Organylsulphinylethyltrifluorosilanes, $RSOCH_2CH_2SiF_3$, have also been synthesized for the first time [141]. ^{19}F and ^{29}Si NMR data have demonstrated the existence of intramolecular coordinate bond Si ← O in these molecules and the non-equivalence of the equatorial and axial fluorine atoms [142].

A study has been made to develop new types of organosilicon monomers containing an SO_2Cl group in the hydrocarbon radical bonded to the silicon atom. The study involved the photochemical sulphochlorination of methylchlorosilanes $(CH_3)_{4-n}SiCl_n$ (n = 1-3) with sulphuryl chloride, and the effects exerted on this process by chlorides and oxychlorides (1 mol. %) of aluminium, tin, phosphorus, antimony, sulphur, selenium, copper, zinc, mercury, vanadium, niobium, tantalum, molybdenum, tungsten, chromium, manganese, iron, cobalt, nickel, yttrium, lanthanum, cerium, neodymium, dysprosium, holmium, and thulium [143].

The photochemical sulphochlorination of methyl(chloro)silanes is attended by a competing chlorination process:

$$(CH_3)_{4-n}SiCl_n + SO_2Cl_2 \xrightarrow{h\nu}$$
$$\rightarrow ClSO_2CH_2(CH_3)_{3-n}SiCl_n + HCl \quad (104a)$$
$$\rightarrow ClCH_2(CH_3)_{3-n}SiCl_n + SO_2 + HCl \quad (104b)$$

The ratio of the products of reactions (104a) and (104b) and the conversion of methylchlorosilane is governed by the number of chlorine atoms (n) in its molecule. The general reactivity of methylchlorosilanes drastically decreases and their tendency to yield chloro derivatives according to scheme (104b) becomes more pronounced with increasing (n). Thus, without catalysts, the conversion of trimethylchlorosilane (n = 1) makes up 70%, while the ratio of sulphochlorination (104a) and chlorination (104b) products is 2.5 : 1. The conversion of dimethyldichlorosilane (n = 2) is much lower (48%), whereas the ratio of the products of reactions (101a) and (101b) equals 1 : 1. The only way in which methyltrichlorosilane (n = 1) reacts with sulphuryl chloride is chlorination (104b), which leads to $ClCH_2SiCl_3$ (7% yield) in 8 to 9 hours (19% yield in 40 hours) [144].

Several of the inorganic chlorides and oxychlorides studied

significantly affect the photochemical reaction between methylchlorosilanes and SO_2Cl_2.

For example, the chlorides of yttrium and those of rare-earth elements of the yttrium subgroup (thulium, holmium, and dysprosium) have a considerable photocatalytic effect on the reaction of sulphuryl chloride with all three of the methylchlorosilanes studied [145]. With these new photocatalysts, the conversion of methyltrichlorosilane, dimethyldichlorosilane and trimethylchlorosilane increases from 7 to 35-53, from 48 to 64-89, and from 70 to 83-99%, respectively.

The effects produced by other photocatalysts found on the reaction between SO_2Cl_2 and $(CH_3)_{4-n}SiCl_n$ depend on the number of chlorine atoms (n) in the molecule of the latter. To illustrate, the conversion of dimethyldichlorosilane in the photochemical reaction with SO_2Cl_2 increases from 60 up to 100% in the presence of SCl_2 (or elemental sulphur) and $MnCl_2$. In contrast, elemental sulphur inhibits the photoreaction of methyltrichlorosilane with SO_2Cl_2. The chlorides of all other elements mentioned promote the conversion of methyltrichlorosilane to chlorine derivatives. Concurrently, all the chlorides and oxychlorides under study, with the exception of YCl_3, $TmCl_3$, and $HoCl_3$, inhibit the interaction of SO_2Cl_2 with trimethylchlorosilane.

The highest yield 60% of the product of sulphochlorination of $(CH_3)_3SiCl$, $ClSO_2CH_2(CH_3)_2SiCl$, was obtained with YCl_3 as a photocatalyst.

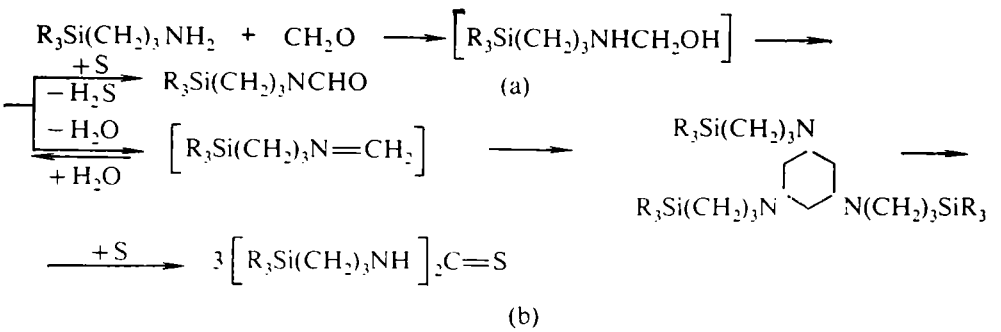
Elemental sulphur, in the presence of which $ClSO_2CH_2(CH_3)SiCl_2$ is produced in 50% yield, has been found to be an effective photocatalyst of the sulphochlorination of dimethyldichlorosilane.

3.4. Compounds Containing the Si—(C)$_n$—N—C=S Group

Among these compounds with $n = 0$ are organylisothiocyanatosilanes $R_{4-n}Si(NCS)_n$. It is most convenient to synthesize them by reacting ammonium thiocyanate with the corresponding organylchlorosilanes and $SiCl_4$ [146]. Trimethylisothiocyanatosilane has also been obtained by the reaction of bis(trimethylsilyl sulphate with NH_4SCN [32] according to scheme (12).

The reaction of 3-(trialkylsilylpropyl)amines with elemental sulphur and formaldehyde in a water-alcohol medium at temperatures ranging from 80 to 90°C yields an equimolar mixture of N-(3-trialkylsilylpropyl)formamide and bis-N,N′-(3-trialkylsilylpropyl)-thioureas, which is difficult to separate. The intermediate product of reaction (105), which is shown below, involves the 3-trialkylsilylpropylazomethine trimers N,N′,N″-tris(3-trialkylsilylpro-

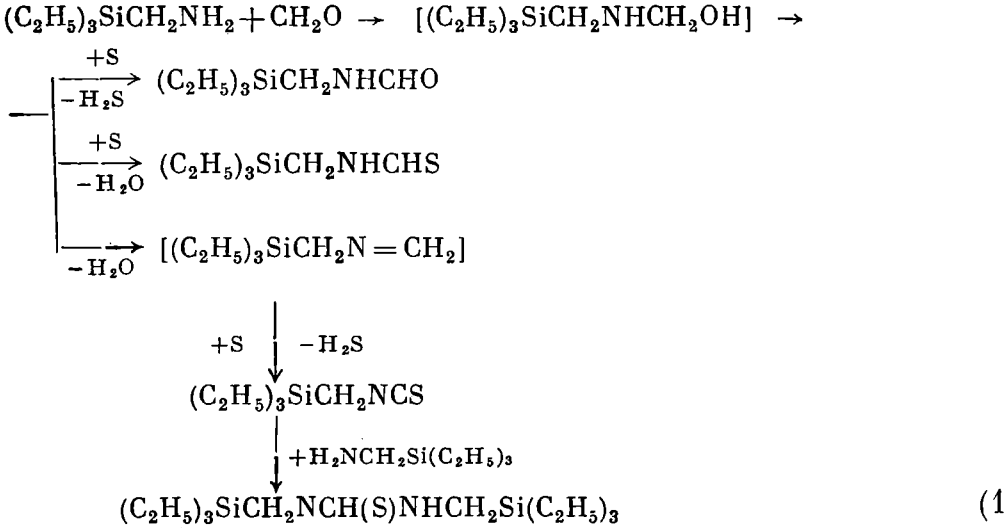
pyl)hexahydrotriazines [147, 148]:



(105)

The reaction of 3-triorganylsilylpropylamines with paraform in benzene, with simultaneous removal of the water formed afforded N,N′,N″-tris(organylsilylpropyl)hexahydrotriazines in high yields (70 to 80%) according to Eq. (105b). Their reaction with elemental sulphur in the melt or in dry alcohol or in benzene offers a convenient method of preparing N,N′-bis(3-triorganylsilylpropyl)-thioureas [149] following scheme (105b).

In contrast to 3-triorganylsilylpropylamines, the reaction of triethylsilylmethylamine with formaldehyde and sulphur in a water-alcohol medium gives N,N′-bis(triethylsilylmethyl)thioureas in moderate yield (10%) [150]. The major reaction product is triethylsilylmethylisothiocyanate (30% yield). In addition to the latter, triethylsilylmethylformamide and triethylsilylmethylthioformamide are formed in 5 and 3% yield, respectively:



(106)

As with 3-trialkylsilylpropylamine, N,N,N′,N′-tetrakis(3-triethylsilylpropyl)thiourea is the major product of the reaction of

N,N′-bis(triethylsilylpropyl)amine with sulphur and formaldehyde in a water-alcohol medium [150]. Along with this product, the reaction yields N,N′-bis(3-triethylsilylpropyl)formamide, N,N′-bis(3-triethylsilylpropyl)thioformamide, and N,N,N′,N′-tetrakis(3-triethylsilylpropyl)urea in minor amounts.

$$(C_2H_5)_3Si(CH_2)_3]_2NH + CH_2O \rightarrow (C_2H_5)_3Si(CH_2)_3NCH_2OH \rightarrow \begin{cases} \xrightarrow[-H_2S]{+S} [(C_2H_5)_3Si(CH_2)_3]_2NCHO \\ \xrightarrow[-H_2O]{+S} [(C_2H_5)_3Si(CH_2)_3]_2NCHS \end{cases} \quad (107)$$

$$[(C_2H_5)_3Si(CH_2)_3]_2NH + HC(S)N[(CH_2)_3Si(C_2H_5)_3]_2 \rightarrow \xrightarrow[-H_2S]{+S} [(C_2H_5)_3Si(CH_2)_3]_2NC(S)N[(CH_2)_3Si(C_2H_5)_3]_2 \quad (108)$$

$$[(C_2H_5)_3Si(CH_2)_3]_2NH + HC(O)N[(CH_2)_3Si(C_2H_5)_3]_2 \rightarrow \xrightarrow[-H_2S]{+S} [(C_2H_5)_3Si(CH_2)_3]_2NC(O)N[(CH_2)_3Si(C_2H_5)_3]_2 \quad (109)$$

Of the numerous products of the reaction of N,N′-bis(triethylsilylmethyl)amine with formaldehyde and sulphur in a water-alcohol medium, only N,N′-bis(triethylsilylmethyl)formamide and hexaethyldisiloxane have been identified. The formation of the latter seems to be due to the α-decomposition of the starting organosilicon amine [150].

It is convenient to synthesize N,N′-bis(triorganylsilylalkyl)thioureas by condensing the corresponding triorganylsilylalkylamines with thiourea in the presence of ammonium sulphate [148]:

$$2X_3Si(CH_2)_nNH_2 + (NH_2)_2C{=}S \xrightarrow{(NH_4)_2SO_4} \rightarrow X_3Si(CH_2)_nNHC(S)NH(CH_2)_nSiX_3 + 2NH_3 \quad (110)$$

$X = C_2H_5,\ C_2H_5O;\quad X_3 = CH_3(C_4H_9)_2$

Attempts to prepare N-organyl-N′-(3-triorganylsilylalkyl)thioureas in a similar fashion from the corresponding Si-containing amines and N-organylthioureas $RNHC(S)NH_2$ were not successful [151]. Again, only N,N′-bis(triorganylsilylalkyl)thioureas are formed as indicated below:

$$2X_3Si(CH_2)_nNH_2 + H_2NC(S)NHR \xrightarrow{(NH_4)_2SO_4} \rightarrow X_3Si(CH_2)_nNHC(S)NH(CH_2)_nSiX_3 + NH_3 + RNH_2 \quad (111)$$

$R = C_6H_5,\quad -CH_2-CH{=}CH_2$

It was not possible either to synthesize N-(triorganylsilylpropyl)-thioureas by the hydrosilylation of N-allylthiourea with triorganylsilanes in tetrahydrofurane in the presence of $H_2PtCl_6 \cdot 6H_2O$ or $(C_6H_5CN)_2PdCl_2 \cdot P(C_6H_5)_3$ [152]. In this case, dehydrocondensation proceeds concurrently with cleavage of the $N—CH_2$ bond in the starting allylthiourea $CH_2 = CHCH_2NHC(S)NH_2$. It is followed by thermal decomposition of the N,N′-bis(triorganylsilyl)ureas formed in the first step of the reaction. The reaction can also occur without a catalyst to yield triorganylsilylisothiocyanatosilanes, hexaorganyldisiloxanes, hexaorganyldisilazanes, propene (or propane with a catalyst), and hydrogen:

$$CH_2=CHCH_2NHC(S)NH_2+2HSiX_3 \rightarrow CH_2=CHCH_3+H_2+$$
$$+[X_3SiNHC(S)NHSiX_3] \xrightarrow{\Delta} X_3SiNCS+X_3SiNH_2 \rightarrow$$
$$\rightarrow 0.5X_3SiNHSiX_3+0.5NH_3 \qquad (112)$$

Unlike allylthiourea, phenylthiourea enters only into the dehydrocondensation reaction with triorganylsilanes. The resulting N-phenyl-N′-(triorganylsilyl)thiourea further decomposes as follows [152]:

$$2C_6H_5NHC(S)NH_2+2HSiX_3 \rightarrow 2H_2+2[C_6H_5NHC(S)NHSiX_3] \rightarrow$$
$$\xrightarrow{\Delta} C_6H_5NH_2+X_3SiNCS+C_6H_5NCS+X_3SiNH_2 \rightarrow$$
$$\rightarrow 0.5X_3SiNHSiX_3+0.5NH_3 \qquad (113)$$
$$X=C_2H_5,\ OC_2H_5$$

N,N′-Bis(triorganylsilylpropyl)thioureas readily react with hydrogen chloride in ether to yield the corresponding isothiouronium salts:

$$[R_3Si(CH_2)_3NH]_2C=S+HCl \rightarrow$$
$$\rightarrow R_3Si(CH_2)_3NHC(S)NH(CH_2)_3SiR_3 \cdot HCl \qquad (114)$$

Previously unknown N,N-bis(3-silatranylpropyl)thiourea has been synthesized by transesterification of N,N′-bis(3-triethoxysilylpropyl)thiourea with triethanolamine [153]:

$$S=C[NH(CH_2)_3Si(OC_2H_5)_3]_2+2(HOCH_2CH_2)_3N \rightarrow$$
$$\rightarrow S=C[NH(CH_2)_3Si(OCH_2CH_2)_3N]_2+6C_2H_5OH \qquad (115)$$

The latter, similarly to its oxygen analogue, reacts with the alcohol formed by the transesterification to produce strong 1 : 1-3 : 1 associates. According to IR spectroscopy, the molecule of N,N′-bis(3-triethoxysilylpropyl)- and N,N′-bis(3-silatranylpropyl)thiourea displays an intramolecular bond between the hydrogen of the NH group and the oxygen to form a seven-membered cycle.

4. BIOLOGICAL ACTIVITY AND PRACTICAL USES

The discovery of the insecticide activity of alkylisothiocyanatosilanes [154] has promoted one of the authors to start research on biologically active organosilicon compounds [155-157]. Further, the toxicity of triorganylsilylalkanethiols, alkyl(triorganylsilylalkyl)sulphides, bis(triorganylsilylalkyl)sulphides, vinyl(trialkylsilylalkyl)sulphides, alkyl(trialkylsilylalkyl)sulphones, bis(trialkylsilylalkyl)thiosulphonates, trialkylsilylalkane sulphonates [158], as well as Si-organylsubstituted silatranes containing the sulphur atom in the substituent R attached to the silicon atom has been examined.

$R^1_3Si(OCH_2CH_2)_m\left[OCH(R^2)(CH_2)_{3-m}N\right]$ $R^1 = R^3S(CH_2)_n$, $CH_3C(O)S(CH_2)_n$,

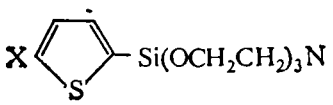
Y; Y = SCH_2CH_2, $CH_2CH_2SCH_2CH_2$

All trialkylsilylalkanethiols and their derivatives, such as sulphides, sulphones, thiosulphonates, and sulphonates, are virtually nontoxic ($LD_{50} > 2.5$ g/kg) when administered intraperitoneally to white mice. The replacement of three alkyl groups at the silicon by methoxy species drastically enhances the toxicity of these compounds. Thus, in going from 2-trimethylsilylethanethiol to 2-trimethoxysilylethanethiol the value of LD_{50} drops from 2500 to 17 mg/kg.

The toxicity of the compounds decreases with an increase in the number of methylene groups (n) separating sulphur and silicon heteroatoms. In going from $n = 1$ to $n = 3$, the LD_{50} value in the series $(CH_3O)_3Si(CH_2)_nSH$ is 17 and 630 mg/kg, respectively, whilst in the series $[(CH_3O)_3Si(CH_2)_n]_2S$, this value varies from 2.2 to 935 mg/kg. The substitution of the methoxy groups at the silicon by ethoxy entities also reduces the toxicity (the LD_{50} value for $R_3Si(CH_2)_3SH$ with $R = CH_3O$ is 630 mg/kg and with $R = C_2H_5O$, 3000 mg/kg).

Transition from alkyl(trimethoxysilylalkyl)sulphides to the corresponding silatranyl derivatives, $R^1S(CH_2)_nSi(OCH_2CH_2)_m \cdot (OCHR^2CH_2)_{3-m}N$ raises the toxicity [101]. In this series the toxicity varies with the values of R^1, n, and m, ranging from 6 mg/kg for 1-(2-ethylthioethyl)silatrane to 3000 mg/kg for 1-(benzylthiomethyl)silatrane. In this case an increase in the number of methylene groups separating the silicon and sulphur atoms in 1-(alkylthioalkyl)-silatranes often enhances their toxicity. This is not the case with alkyl(trialkoxysilylalkyl)sulphides. In particular, in 1-(acetylthioalkyl)silatranes, $CH_3C(O)S(CH_2)_nSi(OCH_2CH_2)_3N$, where an increase in their n number from 1 to 3 reduces LD_{50} from 890 to

20 mg/kg. Finally, extremely high toxicity is exhibited by 1-thienylsilatrane and its 5-substituted



($X = H$, $LD_{50} = 0{,}7$ mg/kg) [103].

Trialkylsilylalkanethiols $R_3Si(CH_2)_nSH$ and the corresponding thiolacetates $R_3Si(CH_2)_nSCOCH_3$ show a sedative action [158]. The products of the reaction of $R_3Si(CH_2)_nSH$ with formaldehyde and amines or alkylenamines—the corresponding aminoalkyl(trialkylsilylalkyl)sulphides—exhibit bactericidal activity towards abdominal typhoid pathogenes (*S. typhi abdominales*) and dysentery (*Shigella Sonnei*) [89].

1-(Alkylthiomethyl)silatrane sulphonium salts act as antiulcerous preparations [119, 159]. The employment of these compounds not only heals gastric ulcers but also cures histamine-induced acute gastritis in animals.

Compounds having biostimulating action have been found among sulphur-containing silatranes. Specifically, 1-(silatranylmethyl)-isothiuronium chloride [160] enhances the silk-productivity of *Bombyx mori*.

As compared with the corresponding 1-(organylthioalkyl)silatranes, 1-(organylsulphenylalkyl)silatranes are not toxic ($LD_{50} =$ $= 5$ and 3000 mg/kg, respectively [161]) and serve as efficient thrombocyte antiaggregants [162]. Organosilicon sulphur-containing compounds of the type $(R^1O)_3Si(CH_2)_nSSnSiR^2_3$ show high bactericidal and fumigant activity [163, 164].

The simple and convenient methods devised to obtain organosilicon sulphur-containing monomers of the type $(RO_3)Si(CH_2)_nCX$, where $X = H$, alkyl, $(CH_2)_nS$, $(OR)_3$, $S(CH_2)_nSi(OR)_3$, $SCH{=}CH_2$, provide strong possibilities of using them as surface-modifying and cross-linking agents, as well as for the development of polymers exhibiting a set of practically invaluable properties. Thus, utilization of trialkoxysilylalkanethiols has made it possible to work up a method of modifying polyvinyl-alcohol and viscose fibers [165]. The very same compounds can be employed for hydrophilizing cotton cloth [166].

The modification of swollen perlite with trimethoxysilylethanethiols as well as bis(trimethoxysilylalkyl)sulphides [167] increases its hydrophilicity and oleophilicity 1.5 times. This considerably reduces the amount of uncompensated charges on the surface, and covers the surface with coatings resistant to the fungi *Aspergillus* and *Penicillium* under tropical climate conditions.

The hydrolytic polycondensation of trimethoxysilylmethanethiol and the copolycondensation with methyltriethoxysilane has produced a series of polyorganylsiloxanes containing thiolic or sulphide groups of the type $[HSCH_2SiO_{0\ 5}]_n$, $[HSCH_2SiO_{0.5}]_n \cdot [CH_3SiO_{0.5}]_m$, $[-SCH_2SiO_{0.5}]_n$, $[-SCH_2SiO_{0.5}]_n \cdot [CH_3SiO_{0.5}]_m$ [168-170]. They are recommended as effective organophilic sorbents. It is worth noting that polymers containing SH groups are selective with respect to organic bases [170]. In addition, they possess cation-exchange and redox properties. Thus, the polymercaptomethylsilsesquioxane [168, 169] is noted for its high reduction capacity (7.6-8 meq/g), and the ease with which it extracts silver, mercury, manganese, iron, cobalt, and nickel ions from solutions. Given pH in the range 0.3 to 11, the polymer is highly selective towards individual metals. For instance, when the pH varies from 0.3 to 3 the polymer extracts silver from solutions containing from 0.003 to 50 mg/litre Ag^+ [171, 172]. The static exchange capacity (SEC) of the polymer for silver is 110 mg/g. A 100-fold excess of zinc(II), lead(II), iron(III), cobalt(II), and nickel(II) ions is no barrier to the quantitative extraction of silver.

The polymer is no less efficient with respect to mercury ions (SEC for mercury is 206 mg/g), which makes it possible to utilize this species for extracting mercury (90-100%) from the industrial discharge of chlorine production [173].

A most convenient and rapid method for determining tin and lead in mineral water has been developed on the basis of polymercaptomethylsilsesquioxane [172]. Synthesis of this polymer and its utilization as an ion-exchanger has laid the foundation for a new trend in applied organosilicon chemistry, namely, the chemistry of ion-exchange and complexing sorbents. The sulpho-acidic ion-exchanger PSK-1 obtained by hydrolytic polycondensation of methyl(chlorosulphonylmethyl)dichlorosilane is highly effective with respect to rare-earth elements [174] and may be recommended to separate lanthanum from other lanthanides. Similar effectiveness relative to rare-earth elements is also exhibited by another organosilicon sulphocation-exchanger PSK-3 [175].

The complexing sorbent poly-[bis(2-silsesquioxanylethylsulphide)] PES-2 holds promise for separating platinum and palladium from osmium [73].

Another complexing sorbent, PSTM-3, is also highly promising in terms of concentration and quantitative separation of traces of precious metals from both environmental media and industrial waste [176, 177].

Bis(trimethylsilyl)sulphate can be employed as a drying agent [178].

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The author treats the material with a view to the latest achievements in colloid chemistry. He deals with the general laws of the physicochemistry of disperse systems and surface phenomena, the science of surface forces and adsorption, the stability of disperse systems, the physical chemistry of high-molecular compounds, micellae formation, and with the properties of powders, suspensions, emulsions, surface films, and aerosols.

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